Application of cathodoluminescence to zircon in FEG-ESEM*

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Abstract Cathodoluminescence (CL) image analysis of zircon is a key step of mineral micro-area compositional investigation and U-(Th)-Pb dating. We introduce a system consisting of field emission ESEM and high performance cathodoluminescence. This system has obvious advantages in imaging resolution and CL spectrum. We acquired some zircon CL images and spectra to demonstrate the ability of this system. Our results show that this system has a great potential application to characterize and identify the genesis of zircon.

Keywords: **zircon, cathodoluminescence, ESEM.**

Zircon, as a stable mineral in physical and chemical properties, plays an important role in the research of rock genesis, diagenesis age, inclusion in (Ultra) high pressure minerals, metamorphic histories and the evolution of orogeny belt[1—4]. In recent ten years, micro-analyses of SHRIMP and LA-ICPMS applied to U-Pb dating have greatly accelerated the research of geosciences. However, in the process of precise analysis, precise localization of analyzed spots and reasonable interpretation of the results must be based on the high quality cathodoluminescence images. Due to the restrictions of low resolution and the sampling methods, the previous cathodoluminescence (CL) systems cannot obtain very clear images. How to acquire high quality images becomes an urgent problem to be solved in geological experiments. In this work, we introduce a high performance CL system consisting of a field emission ESEM and a high performance CL. We will demonstrate the advantages of this system in image resolution and spatial resolution[5]. Using the CL system, we try to acquire high quality CL images and spectra to improve zircon genesis research.

1 Constitution and characteristic of high performance CL system

The high performance CL system consists of a field-emission environmental scanning electron microscopy (FEI, Quanta 200 F) and a spectrograph including panchromatic mode and monochromatic mode (Gatan, Mono CL3+). By using the technique of field emission, the spatial resolution of the environmental scanning electron microscopy (ESEM) is obviously higher than that of conventional scanning electron microscopy (SEM). Since the ESEM can work in two different vacuum modes: low vacuum mode and environmental vacuum mode besides high vacuum mode, the insulated samples can be analyzed directly without coating[6]. Thus, the samples can avoid pollutions and damages. In addition, this equipment provides the ability to record monochromatic images at chosen wavelengths of interest. Therefore, the CL system greatly improves the image quality and the spectrum analysis ability.

1.1 Field emission ESEM

Field emission ESEM is a new advanced SEM in the world. It has some main advantages in comparison with the conventional SEM: it has high spatial resolution, and insulating and biological samples can be observed directly without coating. Owing to the new techniques of field emission gun and pressure-limiting aperture (PLA) adopted in the ESEM, the ability of micro-analysis has been greatly improved.

Field emission gun: The electron gun of the ESEM is a Schottky field emission source. The characteristics of the gun are high brightness and small energy dispersion of the electron beam. Therefore, we can obtain a high quality electron probe through a demagnification unit. The spot size is about 1 nm with a high current density of 1 nA. Thus, the signal noise

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ratio and spatial resolution (< 2 nm) of the image have been improved greatly.

Pressure-limiting aperture: The ESEM uses conventional differential pumping across a pressure-limiting aperture to separate the high vacuum of the electron optics column from the high pressure of the specimen chamber. Quanta 200F has three operating vacuum modes to deal with different types of samples. High vacuum is the conventional operating mode in conventional scanning electron microscopes. The other two application modes are low vacuum and ESEM modes. In these modes the column is in high vacuum while the specimen chamber is in a high pressure range of 0.1 τ— 30 τ (Fig.1). Either mode can use water vapour from a built-in water reservoir, or auxiliary gas supplied by the user gas inlet provided for this purpose. Observation of out gassing or highly charging materials can be made by using one of these modes without metal coating.

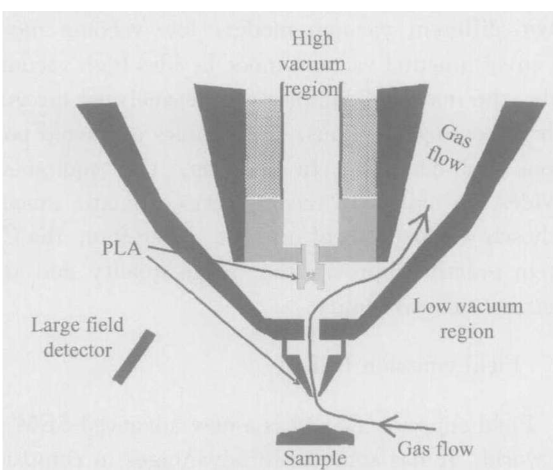

Fig. 1. Schematic diagram of PLA in Quanta 200F.

The elimination of the specimen charging is achieved by the introduction of gas molecule (usually water vapour) in the specimen chamber. The collision of the electron beam with gas molecules produces positive ions near the specimen surface. These ions can be combined with the excess electronic charges on the surface, causing neutralization of the sample surface. The presence of gas around the specimen has some important advantages: the first is to suppress charge accumulation on the insulating specimens; the second is to preserve the natural state of the sample in the electron detection. Fig. 2 shows the experimental results of the Zircon sample without metal coating in different vacuum modes. We can see that the CL images and SEM images of the sample are severely charged in high vacuum mode (Fig. 2(a), (b)) while those in low vacuum mode are clear and have no charging effect. (Fig. 2(c), (d)).

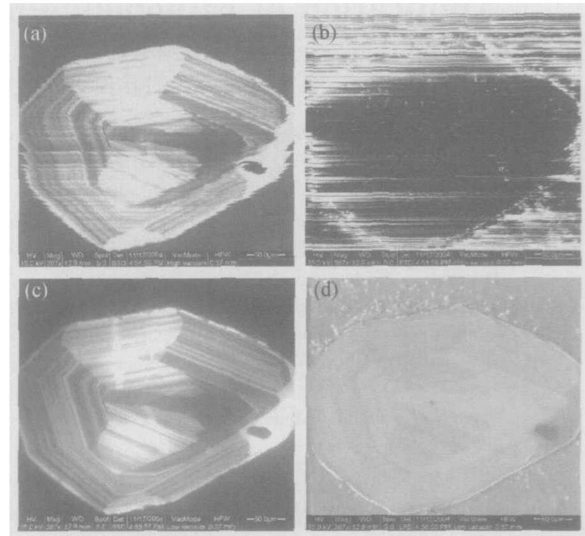

Fig. 2. Comparison of SEM and CL images of Zircon without coating in different vacuum modes. (a) CL image of Zircon in high vacuum mode; (b) SEM image of Zircon in high vacuum; (c) CL image of Zircon in low vacuum mode; (d) SEM image of Zircon in low vacuum mode.

1.2 High performance CL spectrometer

The CL spectrometer (Mono CL3+) consists of CL302 collection, monochromator and high sensitivity photomultiplier. The diamond turned paraboloidal mirror (10 mm in thickness) is a key and delicate optical component in the CL302 collection. There is a hole in the mirror to be coincident with the electron optical axis of the microscope. The CL302 allows precise positioning in the X direction with 75 mm of retraction compatible with the chamber vacuum. Switchable mirrors in the 300 mm Czerny-turner monochromator allow the system to be operated in panchromatic or monochromatic mode. The wavelength is in the range of 200 mm—900 nm. The width of slit is continuously variable from 10 μm to 5 mm. The spatial resolution depends on the grating. In panchromatic mode, the light bypasses the monochromator and is directly coupled to the PMT detector. In monochromatic mode, there are two options depending on the serial/parallel configuration. We can obtain monochromatic imaging and spectrum using the CL spectrometer.

2 CL images and CL spectra of different geneses zircons

Zircons can be found in various rocks of different

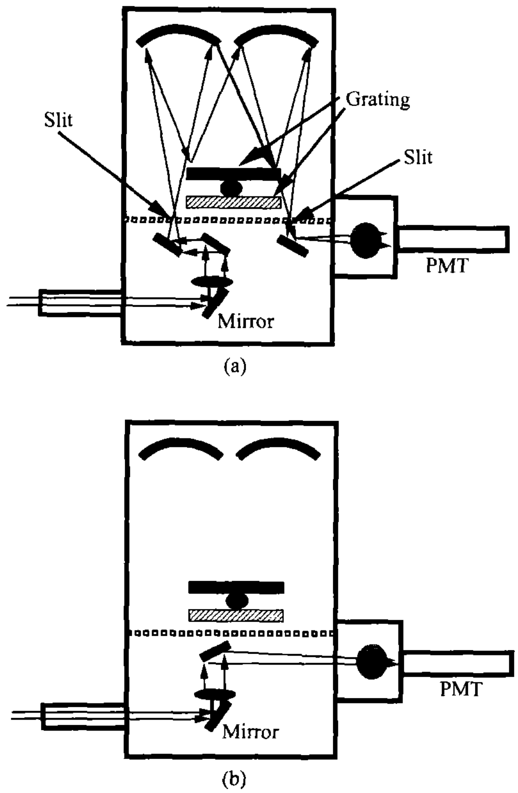

Fig. 3. Schematic diagram of monochromator for monochromatic and panchromatic collections. (a) Monochromatic mode; (b) panchromatic mode.

petrogeneses as an accessory phase. Magmatic zircons apparently differ from the metamorphic ones due to their different crystallizing mechanics[7]. Magmatic zircons are formed under suspending conditions in magmas where zircons can grow freely. As a result, the crystals are usually euhedral to semi-euhedral prismatic and bipyramidic. CL imaging reveals that the grain interior usually has oscillating magmatic crystallizing zonations parallel on the growth boundaries. The width of the zonation relates to the magma temperatures and the element diffusion rates in the crystallize process[1]. The wider oscillating zonations are usually formed at high temperature similar to those of zircons in troctolites and gabbros, while the narrow and dense oscillating zonations are formed in zircons in medium to acidic rocks like granites. In metamorphic rocks, zircons are formed in the recrystallization of Zr and Si released by the decomposition of minerals in metamorphism or influenced by metamorphic fluids. Most of them are metamorphism-accreted zircons with a magmatic core or recrystallized zircons by reworking existing grains in protoliths besides new-grown metamorphic zircons. Generally, zircons have complicated interior structures. Since metamorphism-accreted zircons grow typically in sub-solid and multi-facial ways, they usually have various crystal forms such as round, euhedral, semi-euhedral, and euhedral forms. Various zonations are developed in these zircons including non-zonation, and weak, misty, fan-shaped, fir needles-like, facial, spongy, and streaming zonations[8]. Due to the relatively strong fluorescent effects of zircons, CL imaging of the interior structures becomes the most important method of discriminating the genesis-type of zircons.

2.1 Advantages of high performance CL spectroscope in zircon analyzing

The CL system introduced here consists of a field emission ESEM and a CL spectroscope. It has the following advantages in analyzing the insulating samples such as zircons in comparison with the CL system established on a high resolution microscope, an electronic microprobe, or a conventional SEM:

(1) CL imaging in the low vacuum mode is optional. Because it is unnecessary to coat a metal film on the sample surface, a plain polished section or a thin section can be observed. The investigation can also be performed directly on the naked zircons by attaching it on polished resin such as SHRIMP and LA-ICPMS targets, which enhance the micro-analyzing ability of zircons.

(2) The resolution of the CL system is essentially improved due to the use of field emission ESEM. Since a low energy electron beam was selected as the activating source, the surface damage of our proposed CL system decreased considerably compared with other CL systems, e.g. the surface damage is seldom found in the resin target for SHRIMP U-Pb dating, which guarantees the micro-analyzing of zircons.

2.2 Significance of high- quality CL image

The precise timing of the geological processes is the main task of geology. Based on mineral U-(Th)-Pb isotopic system analyzing, the micro area dating of single mineral grain is becoming more and more indispensable, due to the increasingly developed micro-analyzing techniques such as SHRIMP and LA-ICPMS.

U, Th, and REE-rich zircons and baddeleyites are among the most important minerals used in U-(Th)-Pb isotopic geochronological studies. Zircon CL image can be used to reveal the geneses of zircons with complicated interior structures and to recuperate the zircon crystallizing processes. Thus, reliable bases can be provided for choosing the analyzing sites of micro area dating, reasonably explaining the acquired U-Pb ages, and characterizing the geological events probably undergone in the host rocks of zircons. Therefore, high quality zircon CL image has been a requirement in zircon U-Pb geochronological studies.

We investigate the CL panchromatic and monochromatic spectra of zircons with different geneses using the high-performance CL analyzing system mentioned above. The results indicate that this CL system basically satisfied the study of complicated zircon interior structures. The CL panchromatic images of a baddeleyite (Fig. 4(a)) and a magmatic zircon with two captured earlier zircons (Fig. 4(b)) from Jinchuan copper-, nickel-rich ultramafic rocks in Longshoushan block[9], a metamorphic zircon (Fig. 4(c)) from the granulite in Yushugou terrain, southern Tianshan[10], and a metamorphic zircon (Fig. 4(d)) from the garnet peridotite in North Qaidam UHP belt[11] clearly reveal the complicated interior structures of these zircons and the characteristics of the inclusions including the captured earlier zircons, which provides the confirmed basis for the explanation of SHRIMP U-Pb dating data and their geological implications.

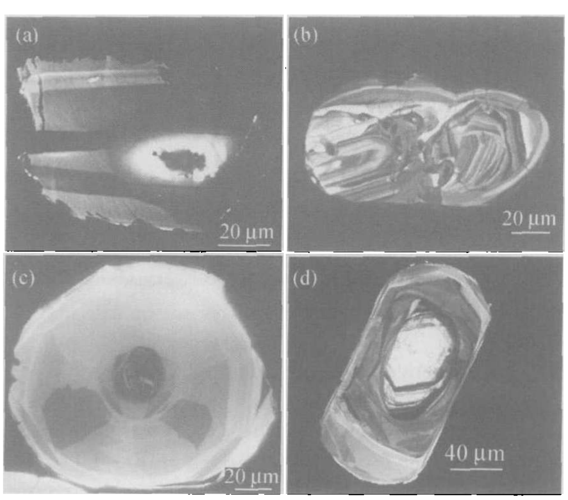

Fig. 4. Baddeleyite and zircon CL images acquired using the high-performance CL system. (a) A baddeleyite from Jinchuan copper-, nickel-rich ultramafic rocks; (b) a magmatic zircon from Jinchuan copper-, nickel-rich ultramafic rocks; (c) a metamorphic zircon from the granulites in Yushugou terrain; (d) a metamorphic zircon from the garnet peridotite in the North Qaidam UHP belt[11].

2.3 CL spectra of zircons with different geneses

Extensive attentions have been paid to many researchers since CL images disclosed the differences in both interior structures[7,8,12] and trace element compositions[13—15] of zircons with different geneses. Recently, we have carried out a primary comparative study on the CL spectra of the zircons with definite magmatic and metamorphism-accreted geneses. The results show that the main luminescence of the zircon emitted at 313, 351, 404(402), 481, 548, 579, 626, 663, and 754(755) nm (Fig. 5). The CL spectra of magmatic zircons form sharp peaks at 481nm and 579 nm(Fig. 5(a), (b)). However, the CL spectra of metamorphism-accreted zircons, such as the zircons in the coesite-bearing gneiss[4] (Fig. 5(c)), garnet peridotite, and eclogite in northern Qaidam basin Yushugou granulite[10] (Fig. 5(d)) in southern Tianshan orogenic belt, and garnet pyroxenite in Songshugou region[16], of Qinling orogenic belt do not form sharp peaks at these wavelengths instead of "wide peaks" at 579 nm and 313—351 nm (Fig. 5(c), (d)).

CL emission may be caused in three ways: (i) Band-band luminescence, i.e. valence electron is excited to the conduction band, and then released to the ground state with the emission of a photon ($h\gamma$), which is the characteristic of the investigating material (Fig. 6(a)); (ii) defect luminescence, i.e. energy relaxation (the return of the excited electron to its ground level) is also possible via other radiative or non-radiative transitions involving local defects (Fig. 6(b)); (iii) impurity luminescence, i.e. some centers might be excited directly in company with relaxation mechanisms. These centers are hardly influenced by the local crystal field, which may often be found for trivalent rare earth element (REE) centers (Fig. 6(c))[17]. The experimental result suggests that the high intensity sharp peaks at 481 nm and 579 nm indicate that the band-band luminescence is predominant in magmatic zircons with euhedral crystal forms, while the prevalent "wide peaks" of zircons with metamorphic geneses relate to the existence of a large number of crystal-facial defects due to the multifacial crystal forms of metamorphism-accreted and metamorphism-recrystallized zircons. The study of Nasdala (2003) on the CL spectra of visible light suggested that the luminescence at 481, 579, and 754 nm can be attributed to the existence of the rare earth element Dy^{3+}, and the luminescence at 579, 626, and 663 nm to the existence of the rare earth element Sm^{3+}. The apparent decrease of intensity at 481 and 579 nm in the CL spectra of metamorphic zircons may relate to the considerable decrease of the heavy rare

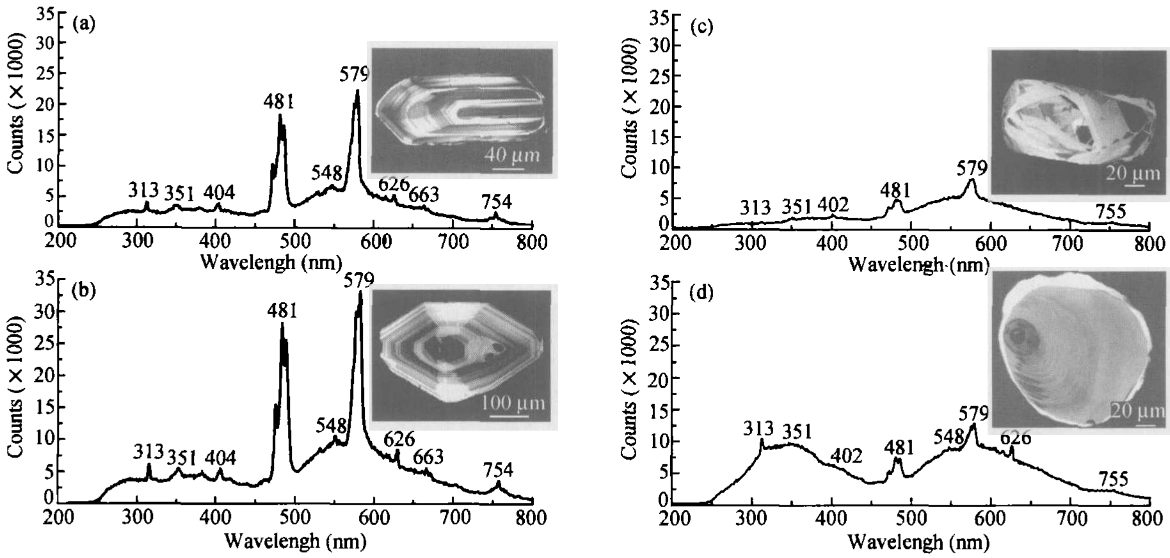

Fig. 5. CL spectra of zircons with different geneses. (a) Magmatic zircon from the H_2O-rich basic complex, northern Qinling; (b) magmatic zircon from the tinge gabbro at Kangksivwa fault belt, Qinghai-Tibet plateau; (c) coesite-bearing zircon from the gneiss in North Qaidam UHP belt[4]; (d) metamorphism-accreted zircon from Yushugou gneiss in southern Tianshan orogenic belt[10].

earth element contents of the zircons[13] in metamorphic rocks, especially the high-grade metamorphosed rocks such as eclogites and granulites. The present study indicates that further studies on the CL spectra may be helpful to recognize zircon geneses and to systematically inverstigate the more complicated interior structures.

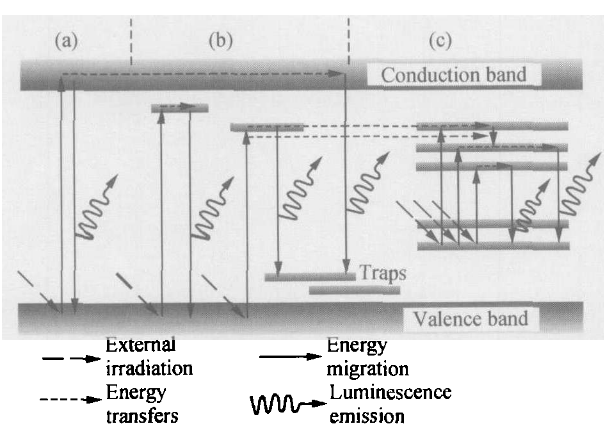

Fig. 6. Schematic diagram of the occurrence of three types of CL. (a) Band-band transitions; (b) band-defect transition; (c) impurity state transitions within forbidden band gaps.

3 Conclusion

The CL system, consisting of a field emission ESEM and a high-performance CL spectroscope, has significant application potential in microscopic analysis, crystal growth condition study, and genesis-type identification of zircons and other minerals. The system, when being combined with the mineral micro area U-(Th)-Pb dating and trace element composition analyzing techniques, will make it possible to precisely determine the timing of tectonic-thermal events, the source of sediments, and the sedimentary ages in geological history.

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