

The Studies of Cathodoluminescence Images and Spectra of Monazite: Potential Application in Lunar Samples. S. H. Yang¹, Q. Zhou¹, G. L. Zhang¹, B. Liu¹, D. W. Liu¹, H. B. Zhang¹, and C. L. Li^{1,1} Key Laboratory of Lunar and Deep Space Exploration, National Astronomical Observatories, Chinese Academy of Sciences, Beijing, China (E-mail: shyang@nao.cas.cn).

Introduction: Monazite, a common phosphate mineral that is rich in rare earth elements (REEs), widely occurs as an accessory phase in crustal rocks. Unlike the Earth, the Moon shows significantly less abundance of monazite than whitlockite and REE-bearing apatite [1]. In particular, lunar monazite would be too small for satisfactory electron probe microanalysis (EPMA).

Cathodoluminescence (CL) is widely used for the microstructure study of many rock-forming and accessory minerals such as zircon and apatite [2]. The most spectacular application of CL imaging is the high-resolution growth textures and other internal structures that are not discernable with other analytical techniques such as back-scattered electron imaging (BSE) or EPMA. The distinct domains in CL images are commonly caused by lattice defects or by the lattice incorporation of several elements (e.g., Mn^{2+} , $REE^{2+/3+}$, Cr^{3+}). CL spectrometry detection limits (less than 50 ppm for Gd^{3+} , Dy^{3+} , Tb^{3+} , or Sm^{3+} , and approximately 400 ppm for Ce^{3+}) are much lower than EPMA analyses [2]. CL spectrometry represents a promising technique for the analysis of trace element concentrations and distributions. The element variation reflected by CL is related to some specific conditions during formation.

The goal of our ongoing work is to study the CL imaging and spectrometry of monazite, hoping that this method can be performed on studying the mineral characteristics and the type and distribution of rare earth elements of lunar monazite.

The CL images characteristic of igneous monazite: The CL images of granite monazites clearly show fine concentric oscillatory zoning and well depicting the genetic type of magmatic monazite (Fig. 1). The dark domain in the rim is possibly related to late-stage alteration or dissolution and is slightly Th-rich, and extremely enriched in Dy, Gd, and Y (Fig. 1).

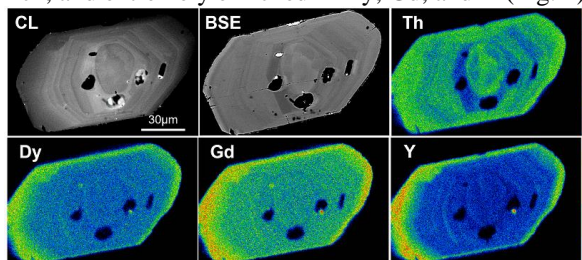


Fig.1. Comparison of X-ray maps, CL images, and BSE images of monazite from two-mica granite sample.

The leucogranite monazite have a more complex internal structure (Fig. 2d-h), which is mainly characterized by broad concentric zoning with locally fine concentric zoning. The good relationships between CL and the compositional variation suggest that the strong CL may be dominated by major elements (P, La, Ce, Nd, and Pr) and minor elements (Sm and Y); however, the elemental concentrations of U, Th, and Si are high, corresponding to the dark domain, in which elements act as impurities and lead to quenching effects (Fig. 3). The zonation characteristics in the monazite CL image of leucogranite likely represent episodic crystal growth and are closely related to the change in major elements from multistage magma material when monazite crystallized, thereby recording the igneous crystallization process.

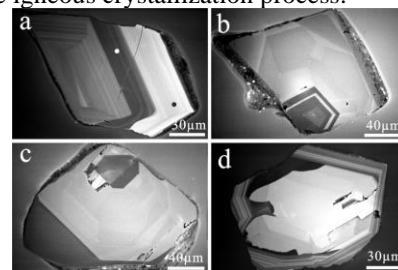


Fig. 2. CL images of igneous monazites from two-mica granite (a-c) and leucogranite (d-h)

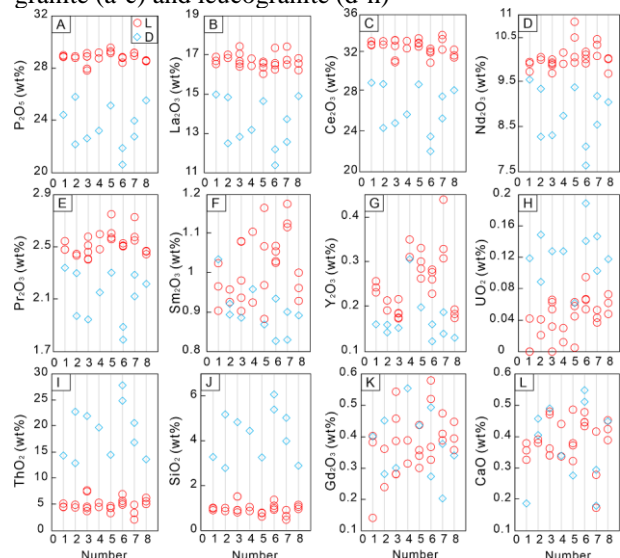


Fig.3. Elemental compositions (wt %) of darker and lighter CL domains in eight representative eight igneous monazites, as determined by EPMA analysis. L: Light CL domain; D: Dark CL domain.

CL activator elements of igneous monazites:

Monazite CL spectra usually show three main broad bands centered at 340, 485, and 640 nm in addition to several narrower bands (Fig. 4a). Deconvolution was carried out on Mzn1 spectra into Gaussian curves which can reveal different activators (Fig. 4b-h). The CL spectra of the monazite are narrow emission REE³⁺ peaks or sets of peaks (Gd³⁺, Tb³⁺, Dy³⁺, Sm³⁺, and Nd³⁺), due to the f-block electrons and are forbidden transitions that are sharp. The broad peaks are most likely intrinsic in origin.

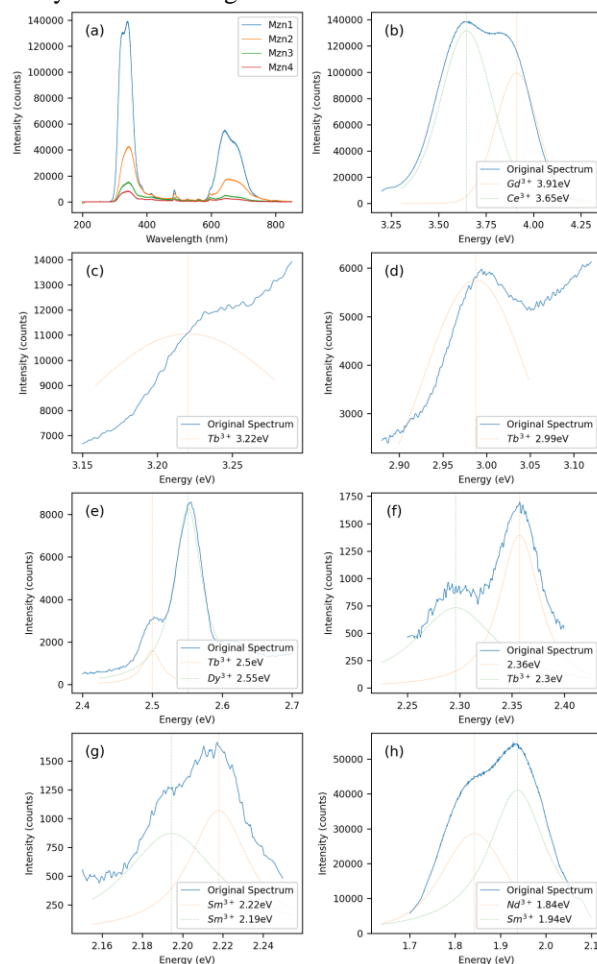


Fig. 4. CL spectra of the monazite. (a) CL spectra on the whole monazite area from both igneous and metamorphic monazites and the spot area of the darker and lighter parts from an igneous monazite; (b-h) Gaussian fitting on Mzn1 CL spectrum. Mzn1 is the black spot area of the lighter part of the monazite in Figure 2a.

Potential applications of CL imaging and spectrometry in lunar monazite:

As outlined above, we are in the process of presenting an analytical method for monazite CL imaging and spectrometry using field emission SEM. The SEM-CL can reveal the internal structure and REE composition of monazite, providing important genetic information. The knowledge of the typomorphic luminescence characteristics of minerals can be used to reconstruct the processes of mineral formation, alteration and diagenesis. This methodology should work on monazite and other REE-bearing minerals in lunar samples.

It has been reported previously that lunar monazites have kinds of types [1, 3-4]. Ce-rich Monazite is usually considered the most abundant REE-bearing mineral. The monazite having more Th abundance may crystal from residual basaltic melt enriched in incompatible REE and Th, indicating its magmatic origin [1]. While thorium-poor monazite occurs as an inclusion in a ferrohedenbergite grain within a mesostasis area of Apollo 11 basalt, showing that the light REE's are relatively very much more abundant than the heavy REE's [3]. The Y and MREE enrichment in monazite could form during metasomatic alteration of primary basalts, accompanied by decomposition of tranquillityite release of Y and MREE. Such monazites with complex REE composition could form at fairly high-temperature conditions and avoid simultaneous occurrence with xenotime (Y, HREE) [PO₄] [1]. Monazite exsolution from apatite based on a symplectite assemblage also indicates its hydrothermal or metasomatic origin [4]. The distribution of specific elements in monazite, like Y, Th, and REEs can be as a tool to discriminate for provenance.

The mesostasis regions in Chang'E-5 basalts are the sites of crystallization of a suite of minerals including whitlockite, apatite, baddeleyite, and tranquillityite, zirconolite and, zircon and monazite [5]. CL imaging and spectrometry presented in its synergistic context may provide not only the characteristics of the internal structure but also REE composition in monazite, and is thus an ideal approach for studying growth history of lunar monazite.

References: [1] Kartashov P. et al. (2006) *Dokl. Earth Sc.*, 407, 498–502. [2] Barbarand and Pagel (2001) *Am. Mineral.*, 86, 473–484. [3] Lovering J.F. et al. (1974) *EPSL*, 21, 164–168. [4] Barnes J.J. et al., (2018) *LPSC*, 2083, 2667. [5] Li C.L. et al., (2022) *Natl. Sci. Rev.* 9, nwab188.