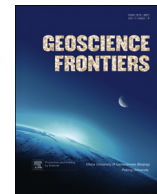


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Research paper

Dating of zircon from high-grade rocks: Which is the most reliable method?

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ABSTRACT

Magmatic zircon in high-grade metamorphic rocks is often characterized by complex textures as revealed by cathodoluminescence (CL) that result from multiple episodes of recrystallization, overgrowth, Pb-loss and modifications through fluid-induced disturbances of the crystal structure and the original U-Th-Pb isotopic systematics. Many of these features can be recognized in 2-dimensional CL images, and isotopic analysis of such domains using a high resolution ion-microprobe with only shallow penetration of the zircon surface may be able to reconstruct much of the magmatic and complex post-magmatic history of such grains. In particular it is generally possible to find original magmatic domains yielding concordant ages. In contrast, destructive techniques such as LA-ICP-MS consume a large volume, leave a deep crater in the target grain, and often sample heterogeneous domains that are not visible and thus often yield discordant results which are difficult to interpret. We provide examples of complex magmatic zircon from a southern Indian granulite terrane where SHRIMP II and LA-ICP-MS analyses are compared. The SHRIMP data are shown to be more precise and reliable, and we caution against the use of LA-ICP-MS in deciphering the chronology of complex zircons from high-grade terranes.

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1. Introduction

Zircon dating by quadrupole LA-ICP-MS has become a common and widespread practice, and large numbers of analyses have been produced in recent years due to the short time required for each analysis and the growing number of zircon geochronology laboratories. This technique has proved reliable in dating relatively simple magmatic rocks with homogeneous zircon populations and has proved most effective in the dating of detrital zircon grains where high precision is not required.

The main challenge for LA-ICP-MS analysis is a reliable correction for common Pb, due to the presence of mercury in the argon gas used in many laboratories to produce the plasma that causes an

isobaric interference by ^{204}Hg on ^{204}Pb (e.g., Andersen, 2002). Such correction is particularly important for samples with low $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. Different methods were developed to overcome this problem (e.g., Horn et al., 2000; Košler et al., 2002; Jackson et al., 2004; Gehrels et al., 2008; Cottle et al., 2009), but most users simply make no correction, assuming that zircon has no or only insignificant common Pb. However, this is often not the case for early Precambrian zircon with a complex history (e.g., Table 4 in Kröner et al., 1989). Alternatively, some users correct for common Pb with a model calculation that assumes a coherent behaviour of Th/Pb and U/Pb and estimates the time of the isotopic disturbance (Andersen, 2002). The crater produced in the zircon by laser ablation, depending on the laser energy density (normally 5–6 Hz and 100 mJ), and assuming about 25–30 pulses during a single analysis, is about 35–40 μm deep (Figs. 1 and 2), thus the technique is rather destructive and, as further discussed below, the deep pit is likely to analyze isotopically inhomogeneous domains in zircon with complex histories. On the other hand, isotopically simple magmatic or metamorphic zircon can be analyzed fast and with high precision due to the large volume ablated.

An alternative, but more expensive and much more time-consuming technique is dating of small zircon domains by a sensitive high-resolution ion microprobe such as SHRIMP II or Cameca

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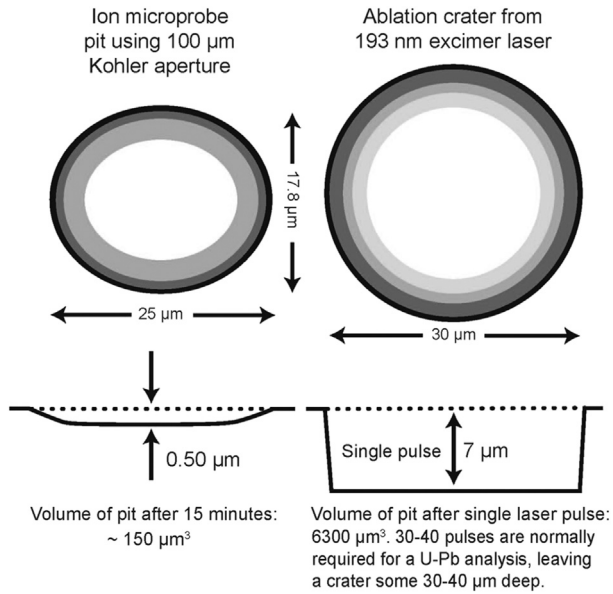


Figure 1. Size of a typical pit produced in zircon by using an ion microprobe during a 15 min analytical run (five cycles) (left) compared to the size of an ablation crater made from about 10 pulses of an excimer laser (right). Bottom drawings show generalized cross-sections of the excavations made by the two techniques (modified from Patchett and Samson, 2011).

1280. The advantage of this technique is the shallow analytical pit, only 1.5–2 μm deep (based on Lee et al., 1997, see Figs. 1 and 2), and the ability to precisely correct for common Pb, whereas the estimate of total U is less precise than using ICP-MS.

Zircon populations from rocks with long and multiphase tectono-metamorphic histories generally do not consist of homogeneous crystals but may contain multiple components such as old cores, surrounded by magmatic overgrowth and further surrounded by metamorphic overgrowth. However, the robustness of zircon without radiation damage, even during ultra-high temperature metamorphism, and the insignificance of Pb-diffusion have been demonstrated in many studies, and careful CL- and trace element-assisted investigations make it possible to extract reliable age data from such grains (e.g., Möller et al., 2003; Kooijman et al.,

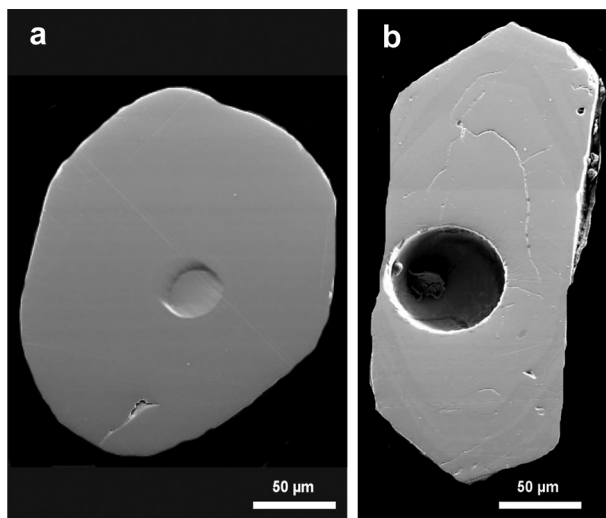


Figure 2. (a) SHRIMP II pit on metamorphic zircon as seen in back-scattered electron (BSE) image; (b) laser pit in BSE image produced after LA-ICP-MS analysis.

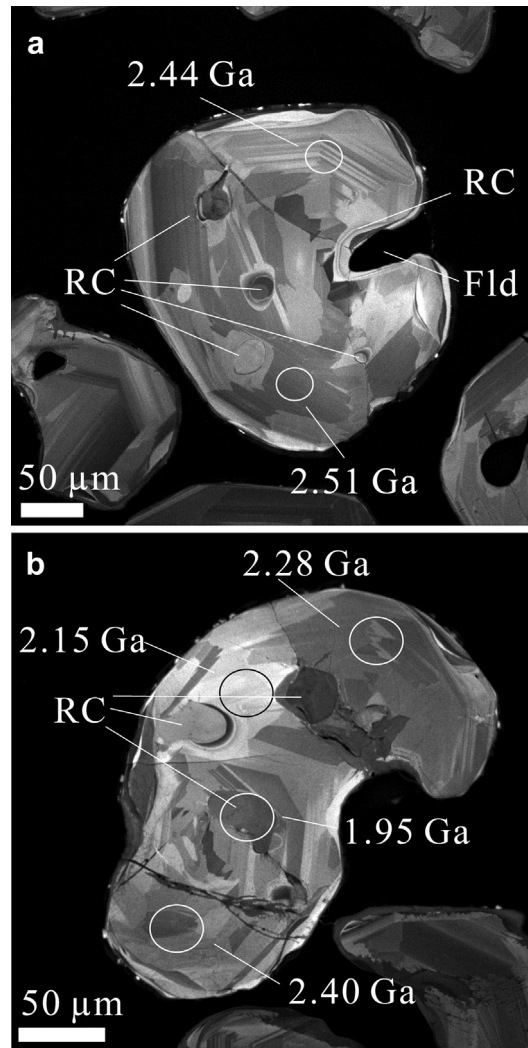


Figure 3. Cathodoluminescence images for zircons from a cpx- and opx-bearing metadiorite gneiss of the high-grade late Archaean terrane in eastern Shandong, North China craton (Wan et al., 2011). These zircons show banded, fir-tree, sector- and/or oscillatory zoning. Positions of SHRIMP II analytical sites with ages (in Ga) are indicated. Note strong luminescence in small, local domains, probably due to recrystallization (RC). Palaeoproterozoic high-grade metamorphism at ca. 1.95 Ga (dark grey, recrystallized domains in a and b) has caused strong recrystallization of magmatic zircon (2.51 Ga, see b) and the formation of new metamorphic domains (b). Ages between 1.95 and 2.51 are due to mixing of igneous and metamorphic components.

2011). In contrast, fluid-induced alteration is common in high-grade metamorphic terranes (e.g., Geisler et al., 2007; Flowers et al., 2010; Wan et al., 2011; Dong et al., 2013; Ma et al., 2012), and recrystallization, combined with Pb-loss, will produce variable discordance in a zircon population, particularly in granulite-facies assemblages (e.g., Corfu, 2013; Kröner et al., 2013). Fig. 3 provides two examples of complex zircon showing evidence of recrystallization within small domains.

More severely discordant data are generally the result of either Pb-loss or mixing of two different zircon phases. Solid state diffusion of Pb from zircon is extremely slow and unlikely to be effective at normal crustal temperatures (Mezger and Krogstad, 1997; Cherniak and Watson, 2001). Therefore, Pb-loss occurs either by extraction of Pb from altered domains by fluids (e.g., Krogh and Davis, 1974, 1975) or by expulsion and/or intragrain redistribution of Pb during recrystallization (e.g., Pidgeon et al., 1998; Connelly, 2001; McFarlane et al., 2005). The former mechanism generally

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