Short communication

Electron microprobe monazite ages from a tin placer deposit on Bangka Island, Indonesia

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ARTICLE INFO

Keywords:
Monazite dating
Electron microprobe
Th-U-total Pb system
Bangka Island
Rare Earth Elements
Tailings

ABSTRACT

A first attempt of Electron microprobe (EMP) based Th-U-total Pb in situ dating of monazites in tailings from a placer deposit (quartz bearing sands) from Bangka Island, Indonesia, revealed for the first time from a single locality in Indonesia an age cluster around 231 Ma as well as two single grains with ages of 1133 Ma and 1916 Ma. The monazite ages from this study agree with detrital zircon ages and whole rock isochron ages from magmatic intrusions, which were reported from various localities all over the Malaysian peninsula, Myanmar and Thailand but not yet from Bangka Island. Perhaps intrusions in the closer vicinity, which could be the source of the monazite under study, have not been discovered so far or the sedimentary catchment area of the placer deposit is much larger than assumed so far. The existence of the monazite ages investigated in this study may also raise the question of the paleogeographic position of Bangka Island and the relative timing of sedimentation and Miocene rifting. However, the present work is an excellent example for the resistance of monazite and its Th-U-Pb system to sedimentary processes and hence is a useful tool for provenance studies and source of Rare Earth Element (REEs) recovery. An important outcome of this study is that sedimentary monazite relics often provide a wide range of unrealistic ages. Such dates may be wrongly explained in terms of recrystallization along with metamorphic process, instead these ages are only a methodic artefact because monazite relics are either not thick enough for dating or show poor surfaces with numerous cracks.

1. Introduction

Monazite, a solid solution of monazite sensu stricto (LREEPO₄), cheralite (ThCa(PO₄)₄), huttonite (ThSiO₄) and xenotime (YHREEPO₄) (Spear and Pyle, 2002), has attracted an enormous interest among geologists because of its great potential for geochronology. The robust Th-U-Pb system of monazite (Parrish 1990, Cherniak and Pyle, 2008) allows a precise determination of crystallization ages by means of chemical dating with the electron microprobe in thin sections (Suzuki et al. 1991, Montel et al. 1996, Suzuki and Kato, 2008). A challenging facet of monazite is that these REE bearing minerals show a certain relic behaviour in nature. Monazite relics may be either detrital (Williams 2001, Krenn et al. 2008), or represent metamorphic/magmatic grains inherited from earlier metamorphic cycles (DeWolf et al. 1993, Forster et al. 2000, Foster et al. 2000, McFarlane and Frost, 2009). Monazites in quartz-rich tailings from abandoned tin mines on Bangka Island, Indonesia, were reported in the past only by Szamatek et al. (2013) and Zglinicki et al. (2020), who studied this mineral in detail with respect to its morphology, chemistry and potential of REEs source. The site
ages presented were calculated for the first time on monazite from a placer deposit, thus providing information about their source, genesis and geochronological significance in the Malaysian peninsula and the Island of Sumatra. The application of the U-Th-Pb dating can be applied, worldwide, to similar REE deposits providing information on the genesis of monazite. In this paper, the author demonstrates the relic behaviour of monazite along with sedimentary processes offering the possibility to use monazite for provenance studies. Furthermore, the enrichment of monazite in the quartz sands offers an enormous potential economic resource for Rare Earth Elements (REEs) in South East Asia and in other similar deposits around the globe. This study should be considered as a first attempt to date monazite from tin placer deposits in this region.

2. Geological setting

Tectonically Bangka Island is characterized by events of subduction and accretion of terranes as reported by Zglinicki et al. (2020) and reference therein. The result of these processes was the emplacement of three granite provinces as described in detail by Schwartz et al. (1995). The island ends the "tin belt" which extends from Thailand to Indonesia (Schwartz et al. 1995). The geology of Bangka Island is characterized by sedimentary sequences as well as major and minor batholiths as reported by Ko Ko (1986). The samples investigated in this study were collected in the location shown in Fig. 1.

3. Methods and sample description

Eight quartz rich tailings, former cassiterite sands, from an abandoned tin mine on the Bangka Island (Indonesia) were investigated by means of electron microprobe (EMP) using back-scattered electron images (BSE images), phase identification with an energy-dispersive system (EDS) as well as dating and chemical analyses using the wavelength-dispersive system (WDS). The location and sampling procedure are described in Purwadi et al. (2019). The site of the study area is close to the areas examined by Zglinicki et al. (2020), who ascribe the tailings to the Tempilang formation, which is described in detail by Ko Ko (1986) and references therein. The tailings were analyzed as grain mounts of quartz rich tailings (including accessories and monazite) in order to detect the minerals and the monazite occurrence, i.e. if embedded in quartz or as discrete grain (see Fig. 2 b, e and f). Grain mounts of quartz rich tailings were selected for the ultra-polished thin sections. Monazite analyses were carried out with a JEOL Hyperprobe JXA-8530F PLUS electron microprobe at the German Centre for Geosciences (GFZ), Potsdam Germany, following widely the procedure described by Förster et al. (2000). An accelerating voltage of 15 kV was used for the measurements in order to minimize damage and/or destruction of the monazite grains. Thorium (Th) was counted 100 s on peak and measured on ThMX while uranium (U) and lead (Pb) were counted 200 s on peak and measured respectively on UMB and PbM resulting in detection limits of 200 ppm for thorium and uranium and around 150 ppm for lead. The counting times on peak for silicon (Si) were 10 s, for calcium (Ca) and phosphorus (P) 20 s and for REEs and yttrium (Y) 50 s. Stoichiometry, composition and ages of analyzed monazite were checked on in-house monazite standard from Madagascar analyzed in different laboratories. The chemistry is described in Montel et al. (1996). A second set of measurements on monazite with the same conditions were performed in the same laboratory.

The samples are dominated by up to 2 mm large, irregularly shaped (broken) quartz (~99 wt%) as well as 5 to 200 µm large, relatively fresh (poorly altered) subhedral accessory minerals either included in quartz or at the grain boundaries. The following accessories were detected: arsenite, cassiterite, ilmenite, rutile, K-feldspar, apatite, zircon, monazite, xenotime, thorite, and uraninite. Monazite are extremely variable in size, shape and surface: the grains are on average ca. 10–150 µm long, sub- to anhedral, partly show straight grain boundaries (Fig. 2 a, b) partly are irregular and embayed (Fig. 2c). In general many of the monazite show cracks and scratches as well as edges and oblique surfaces as result of sedimentation and/or polishing. The monazite grains under study occur mostly as individual grains enclosed either in quartz or at quartz grain boundaries (Fig. 2d, e, f). Some monazite are intergrown with apatite and/or thorite as shown in Fig. 2g or they enclose tiny (1–5 µm), bright thorite grains (Fig. 2g). The monazite shown in Fig. 2g was not selected for dating. Monazites are either unzoned (Fig. 2h) or show diffuse patchy zoning, which for lack of significant chemical variation is an artifact of transport or polishing (Fig. 2a). The monazite in the BSE images are similar geochemically to those described

![Geological map modified after Barber and Crow (2009) with the sampling location (blue star). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
Fig. 2. Back Scattered Electron (BSE) images of Monazites from Bangka Island, Indonesia: (a) Triassic monazite with straight boundaries where the fractures are likely formed during the emplacement of the tin placer deposit or might have occurred after polishing; (b) Monazite (Mnz) embedded in quartz (Qz) not dated; (c) Paleoproterozoic monazite with polishing induced fractures; (d) Triassic monazite with cracks induced by transport or polishing; (e) small Triassic monazite included in quartz; (f) Triassic monazite at quartz grain boundary; (g) monazite (not selected for dating) intergrown with apatite (Ap) and thorite (Thr); (h) round shaped Mesoproterozoic (1133 Ma) monazite. Mineral abbreviation after Whitney and Evans (2010).

in more detail by Zglinicki et al. (2020) and Szamałek et al. (2013). In general, the chemical analyses show little variation within each grain but vary from monazite to monazite as result of magmatic fractionation.

4. Monazite dating, chemistry and age of monazite

The monazite dating campaign includes single point analyses from 22 grains. Three to five analyses were performed per grain. Each of the single point analyses was repeated for five times in the immediate vicinity of the previous measurement. As it will be discussed later in more detail, a couple of single point ages could not be reproduced within the five repetitions and hence were not considered for dating. Single monazite dates, weighted average ages and isochron trends were calculated utilizing the method of Montel et al. (1996) and Isoplot 2.49 (Ludwig, 2001). The statistical distribution of measured monazite ages shows one age cluster and additionally two grains of Proterozoic ages. The weighted ages, isochron trend line and an overview of the chemistry are presented in Table 1. The dominating age cluster is Triassic and defines an isochron (Fig. 3a, Th° vs. total-Pb diagram after Suzuki et al. 1991) with a slope of 0.0102x ± 0.0002, an interception value of −0.00016, an isochron age of 231 ± 5 Ma and a weighted average age of 230 ± 7 Ma. Chemically they show a wide spread values of Y2O3 (up to 3.6 wt%) and ThO2 (3.2–16 wt.% percentage respectively). UO2 ranges from 0.05 to 0.8 wt%. The ratios of Th/U are high and range between 13 and 65. The huttonite (Hutt) values (Th(U) + Si ⇔ REE + P) as well as the cheralite (Chr) contents (Th(U) + Ca ⇔ 2 REE) are variable and range up to 15 mol% Hutt and 13 mol% Chr. According to the monazite-xenotime miscibility gap thermometers of Heinrich et al. (1997) and Pyle and Spear (2000) the highest xenotime value of 0.1 mol Xtm (xenotime) indicates minimum formation temperatures of at least 655 °C (thermometer of Pyle and Spear, 2000) and 738 °C (thermometer of Heinrich et al. 1997) respectively. No significant trend can be observed in the diagram shown in Fig. 3b where the Triassic age is plotted versus the xenotime (Xtm). A Mesoproterozoic age was obtained from a single, 60 µm large monazite grain with a round shape, smooth rims (no embayment, resorption) and a homogenous surface without noteworthy cracks and without any inclusion (e.g. thorite) as shown in Fig. 2h. Seven analyses were carried out throughout the grain providing single point ages from 1116 to 1152 Ma, which define a Mesoproterozoic weighted average age of 1133 ± 48 Ma. Y2O3 ranges from 1.66 up to 2.55 wt%, ThO2 from 4.77 to 5.41 wt% and UO2 up to 0.69 wt%. Unlike the younger monazite generation described above, the Th/U ratios are much lower (8–13) and the integration of the actinides (Th, U) occurred mainly via the cheralite substitution (8.1 to 9.2 mol%) while the huttonite values are around 1 mol%. The highest xenotime value of 0.09 mol Xtm of the Mesoproterozoic grain indicates a minimum formation temperature of 672 °C (Heinrich et al. 1997) and 461 °C (Pyle and Spear, 2000).

Table 1

Overview of the isochron, weighted ages and relevant chemistry for the U-Pb-Th dating.

| Monazite isochron age (Ma) | Monazite weighted age (Ma) | Y2O3 max wt.% | ThO2 range wt.% | UO2 max. wt.% | Hutt1 max. mol % | Chr2 max. mol % | Xtm3 mol |
|---------------------------|---------------------------|----------------|----------------|---------------|----------------|----------------|---------|
| 231 ± 5 Triassic          | 230 ± 7 Triassic          | 3.6            | 3.2–15.9       | 0.8           | 15             | 13             | 0.1     |
| –                         | 1133 ± 48 Mesoproterozoic | 2.55           | 5.41           | 0.69          | 1              | 9.2            | 0.09    |
| –                         | 1962 ± 71 Paleoproterozoic| 0.31           | 5.82–6         | 0.25          | 2              | 7              | 0.09    |

1 Huttonite (Hutt).
2 Cheralite (Chr) according to Whitney and Evans (2010).
3 Xenotime (Xtm).
A Paleoproterozoic weighted mean age of 1916 ± 48 Ma was obtained from another ca. 70 µm large monazite grain (Fig. 2c), which shows a very weak zoning with a slightly brighter core and a bit darker rim with slightly lower Th values (see below). Although the grain reveals irregularly shaped, embayed grain boundaries, the surface is homogeneous without inclusions. Two analyses from the center of the monazite and three analyses performed at the rim show indistinguishable single ages between 1815 and 1962 Ma. The Mesoproterozoic grain is characterized by a low Yttrium (0.28 up to 0.31 wt% Y₂O₃) and shows Th-values from 5.82 to 6 wt% ThO₂, U-values at around 0.25 wt% UO₂ and Th/U ratios ~ 25. The huttonite and cheralite values scatter ~ 2 mol% and 7 mol% respectively. The monazite-xenotime miscibility gap thermometers provide low minimum growth temperature (<300 °C). No isochrones were calculated for the Proterozoic grains due to the low number of analyses and limited Th spread.

5. Discussion

An important outcome of this study is that sedimentary monazite relics are extremely difficult to date by means of EMPA. A couple of analyzed areas in monazite provided ages which either could not be reproduced within the five repetitions and/or showed a significant age deviation between analyses with focused or defocused beam. During a first dating campaign where only a focused beam was used, the author received Cretaceous, Permian and Jurassic ages from some of the sedimentary monazite relics as shown in Fig. 4a and b. These ages could be reproduced during a second and even a third repetition carried out at the same spot but not if the position is changed or the spot was analyzed with a defocused beam. Overall, a defocused beam provided a much better reproducibility as well as more constant beam current during analyses. Obviously, some monazite relics were not thick enough to guarantee a constant beam current during the measurements or the poor damaged monazite surfaces hampered a reliable determination of the analyzed volume. Analyses and consequent reliable ages can be calculated based on the following established procedure: the author searched several areas that appear rather planar and these grains were analyzed with a defocused beam in three to five areas where each analysis was repeated five times. All analyses measured with this procedure resulted in consistent overlapping ages (see Fig. 3a and b). As it will be discussed below in more detail, the monazite features such as fractures, broken

![Fig. 3. Th*vs Pb isochron of the Triassic monazite generation and Xtm vs age diagram: (a) isochron for the Triassic monazite (void squares) (b) Xtm (xenotime) vs age diagram of the Triassic monazite generation.](image)

![Fig. 4. Th*vs Pb isochrones of the four monazite generations based on the analyses where the polishing effect was not considered. (a) isochrones for the Triassic monazite (crosses) and Cretaceous monazite (black squares); (b) isochrones for Permian (circles) and Jurassic (void squares) monazite.](image)
edges, patchy zoning and inconsistent ages is an artifact from the sedimentation and/or polishing rather than from metasomatism.

From the EMP measurements it appears that all parts of monazite grains formed at the same event and as carefully described below the Th-U-Pb system was not disturbed essentially later. This approach is supported by the fact that the studied basement shows only magmatic intrusions (e.g., Ko Ko 1986, Wai-Pan Ng et al. 2017) and no metamorphic imprints (Wan 2020 and references therein) strengthened by the lack of metamorphic phases in neighboring placer deposits (Zglinski et al. 2020). Thus, there appear to be no significant metamorphic events, which could have caused recrystallization of monazite, and or disturbance of the Th-U-Pb system as is reported elsewhere (e.g., McFarlane and Frost, 2009). However, one should consider that monazite formation and/or recrystallization may also have occurred along with metasomatic, sedimentary and/or diagenetic processes (e.g., Read et al. 1987, Wilby et al. 2007, Seydoux-Guillaume et al. 2012). A sedimentary and/or diagenetic formation of monazite under study is unlikely as such grains are often very small and extremely depleted in Th. This is absolutely not the case in this study (see table 1 and Fig. 2 a b c d e and h; monazite in Fig. 2 g was not selected for dating). On the other hand some monazite grains indeed may show evidence for metasomatism and probably have disturbed a Th-U-Pb system, hence were avoided for dating. These grains either contain numerous tiny, bright thorite grains (Fig. 2 g, not selected for dating) as was described also by Szamalek et al. (2013) from detrital monazite form neighboring placer deposit or are intimately intergrown with apatite, thorite and sometimes with xenotime as well (see Fig. 2g). Tiny thorites may have formed metasomatic along with magmatic cooling because of different solubility of actinides and REEs (e.g., Hetherington et al. 2010 and, Seydoux-Guillaume et al. 2012). The latter authors remark that the metasomatically overprinted areas always have lower Th values and considerably higher Th/U ratios relative to the unaffected zones and further provide unrealistic EMPA ages. The diffuse, patchy-like zoning observed in several grains of the present study as well as the embayed grain boundaries and fractures result rather from sedimentary transport and/or from polishing than from metasomatism. This argumentation is supported by the fact that the variation of Thorium and Th/U ratios in different patches is much lower than reported from metasomatic domains by Seydoux-Guillaume et al. (2012). However, intergrowths of monazite, thorite and apatite is not necessarily of metasomatic origin but can also be a primary, magmatic feature or formed during diageneric or sedimentary processes due to the lower Th- and Y- uptake capacity of monazite at low temperature. However, a magmatic origin of detrital monazite is not only compelling from the geological environment but can also be concluded from the high Th and Y contents, indicative of high formation temperature conditions (e.g., Zhu and O’Nions, 1999, Pyle et al. 2001, Heinrich et al.1997), and the high Th/U ratio in monazite, a common feature of magmatic monazite (Janots et al. 2012, Mannucci et al. 1986). Minimum formation temperature of at least 655–738 °C for the Triassic monazite obtained from monazite-xenotime miscibility gap thermometers of Heinrich et al. (1997) and Pyle and Spear (2000) are in good agreement with monazite growths under magmatic conditions. Lower xenotime values in other monazite can be explained because monazite did not gain equilibrium with xenotime. A magmatic origin of detrital monazite from an adjacent placer deposits was already concluded by Zglinski et al. (2020) and Szamalek et al. (2013) based on the chemical composition of monazite, their morphology and zoning. Comparably to our study, Zglinski et al. (2020) and Szamalek et al. (2013) describe up to 200 um large, Th and Y rich monazite with diffuse (patchy), sector and oscillatory zoning as well as high Th/U values. From the current study, it can be deduced that the majority of monazite in this study represent magmatic relics and all parts of monazite grains formed during the same event, except the outermost parts of some monazite crystals, which show resorbed grain boundaries or domains with tiny thorite exolutions.

The occurrence of three different monazite generations in placer deposits from Bangka Island argues for the complex sedimentation history of the studied area, the extremely relic behavior of monazite along with sedimentary processes and the extraordinary stable Th-U-Pb isotopic system that is resistant to Pb loss and thermal resetting (e.g., Parrish 1990, Cherniak and Pyle, 2008). Prior to this study, only Rb/Sr and K/Ar whole rock isochron ages of 217 ± 5 Ma, 214 ± 4 Ma and 74 ± 2 Ma were available from Bangka Island (Priem et al. 1975). These Triassic ages were also observed in the present study but unfortunately Cretaceous monazite were not found either for statistic reasons or because the Cretaceous batholiths are not spread enough in the area. The lack of Proterozoic ages could be explained by the fact that Bangka Island contains a couple of magmatic bodies (Schwartz and Surjono, 1991; Ko Ko 1986), which have not been dated so far. More ages from magmatic intrusions are available from Sumatra, Malay peninsula and the Tin Islands in the the age compilation of Setiawan et al. (2017) and Cobbing (2005). Possibly the Proterozoic magmatic bodies have not been found and dated yet or the source of the sedimentary catchment of placer deposits enclosed a larger area possibly extending more to the north. A few hundreds of kilometers north to the Bangka Island, from the central part of Sumatra, Zhang et al. (2018) report Proterozoic detrital zircon ages of 1010 to 1250 Ma. From the southern Malay peninsula, also several hundreds of kilometers to the north, Sevastjanova et al. (2011) report detrital zircon ages of 1178 ± 44 Ma and 1827 ± 38 Ma. The latter ages are exactly those Proterozoic ages found in our study. Furthermore, Sevastjanova et al. (2011) report detrital Permian zircon ages of 272 ± 6 Ma 281 ± 6 Ma 289 ± 6 Ma. The Permian ages described Sevastjanova et al. (2011), Setiawan et al. (2017) and Cobbing (2005) could not be confirmed in the monazite under study. However, the existence of Permian monazite in the area cannot be excluded. Unfortunately, the current dataset and the lack of further intrusion ages hampers a more detailed discussion of the provenance history and the sedimentary catchment area of the placer deposit. The author believes that more systematic dating studies in the area could provide a larger dataset including more ages. However, the monazite ages, in particular the Proterozoic ages, may also raise several questions concerning the relative timing of sedimentation and rifting which, according to literature, should be of Miocene age (Barber and Crow, 2009). Probably placer deposits formed before and not after rifting as was previously supposed (e.g., Schwartz et al. 1995, Barber and Crow, 2009). Possibly the paleogeographical position of Bangka Island was more to the north of its present location and placer deposits formed before rifting. However, in any case, the present study exemplifies the enormous relict behavior of monazite and hence the great potential for the use of monazite for geochronological and provenance studies. It is also a first attempt to date monazite from tailings recovered in placer deposits considering the effect of polishing and additional dating campaigns should follow to enlarge the monazite geochronological dataset in the region.

6. Conclusions

The current study presents for the first time three electron microprobe (EMP) Th-U-total Pb ages from a tin placer on Bangka Island as well as the enormous difficulties in dating sedimentary monazite by means of EMP. This work highlights the withstand of monazite and its Th-U-total Pb system to sedimentary processes which makes this mineral an indispensable tool for provenance studies and source of Rare Earth Element (REEs) recovery. However, a crucial outcome of this dating campaign is that sedimentary monazite relics often deliver a wide range
of unrealistic ages because they are thinned out and/or show poor surfaces with numerous cracks and irregular edges. Nevertheless, a couple of these monazite relics anyway can be dated reliably if an intelligent dating strategy is applied considering among others a defocused beam, a permanent control of the beam current and numerous repetitions of the analysis spots in the close vicinity. Neglecting this procedure causes incorrect ages which easily may be interpreted in terms of recrystallization along with sedimentary, diagenetic or metasomatic processes.

CRediT authorship contribution statement

Fiorezza Deon: Investigation, Formal analysis, Resources, Validation, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

I would like to thank Oona Appelt, GFZ Potsdam Germany, for the assistance during the EMP measurements. My gratitude goes to Imam Purwadi, Caroline Lievens and Harald van der Werff from the University of Twente the Netherlands for providing the tailings samples. Furthermore, appreciation goes to Franziska Wilke, GFZ Potsdam Germany, for her advice as head of the EMP laboratory during the measurements. The support of Erwin Krenn is also highly appreciated for the preparation of her advice as head of the EMP laboratory during the measurements. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jseaes.2021.104844.

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