

## Invited article

# U–Pb isotope dating and geochemistry of accessory and ore minerals: advances in methods and applications for critical raw material research in Bulgaria

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**Abstract.** The study presents recent advances in the development of U–Pb isotope dating and geochemical tracing of accessory and ore minerals, along with their applications in research on critical raw materials (CRMs). The power of high-precision CA-ID-TIMS U–Pb dating is demonstrated through the bracketing of economic mineralization in porphyry-copper deposits in Bulgaria. LA-ICP-MS dating of zircon, monazite, titanite, Ca-garnet, columbite-tantalite, wolframite, cassiterite, and rutile has contributed to constraining the timing of magmatic, metamorphic, and sedimentary processes, as well as the formation of various CRM deposit types, including magmatic-hydrothermal systems, pegmatites, and bauxites in Bulgaria, with additional examples from other countries. Geochronological results are integrated with trace-element data from the dated minerals to better constrain their sources and to estimate the conditions favourable for metal enrichment, transport, and deposition.

**Keywords:** U–Pb isotope dating, LA-ICP-MS, accessory/ore minerals, trace elements.

## Introduction

Absolute timing obtained through different isotope systems and analytical techniques has become a fundamental approach in geological research worldwide. The application of isotope methods is crucial for dating minerals in all rock types – magmatic, metamorphic, and sedimentary – and for understanding processes such as magma ascent, mixing, recharge, and storage, as well as for correlating geological complexes. In magmatic–hydrothermal systems, focused mineral deposit studies have demonstrated that isotope dating is essential for reconstructing the sequence of processes leading to ore formation and preservation (e.g., Heinrich, 2024). Common geochronological techniques used to define the stages of magmatic–hydrothermal ore deposit evolution include U–Pb dating (applied to

minerals such as zircon, titanite, rutile, columbite-tantalite, Ca-series garnets, wolframite, and other U-bearing phases), Re–Os dating (for molybdenite, arsenopyrite, and pyrite), and Ar–Ar dating (for potassium-bearing alteration minerals such as micas and feldspars) (Chiaradia et al., 2013). Among these methods, the U–Pb technique has proven to be the most robust and broadly applicable. Moreover, U–Pb geochronology can be integrated with trace-element data from the dated minerals (e.g., zircon), providing a powerful tool for geological exploration and mineral system characterization (Dilles et al., 2015; Lu et al., 2016; Wade et al., 2022; Klimentieva et al., 2022; Li et al., 2023). In this study, we focus on U–Pb dating and mineral-tracing techniques and present recent methodological developments and applications worldwide, with particular emphasis on examples from Bulgaria.

## Applications and advantages of the U–Pb dating and tracing techniques

The U–(Th–)Pb method is based on the complex decay of  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$ , which transform into  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$  with half-lives of  $4.468 \times 10^9$ ,  $0.7038 \times 10^9$  and  $14.010 \times 10^9$  years, respectively. The method is considered reliable with the advantage for an internal control of the isotope systems, since the results of the three independent decay series can be used and compared. Due to many natural (e.g. distribution of uranium-bearing minerals with insignificant initial content of common lead) and analytical-technical (type of analytical equipment, spike solutions, external standard reference material, etc.) reasons, isotopes of the two uranium series are most often used for dating.

The applications of U–Pb geochronology are diverse and include dating of igneous and metamorphic events throughout the Earth’s history (from >4000 Ma to <1 Ma); calibrating the geological time scale; determining rates of continental crust production; establishing the provenance of sedimentary rocks, volcanic ash and dust, and river sand; dating ore deposits; and constraining the ages of meteorites. In this contribution, we focus on selected aspects of the development and application of U–Pb dating techniques that improve our understanding of the timing of magmatic–hydrothermal and sedimentary deposits, pegmatites, and skarns, as well as their potential links to ore location and grade.

The role of time in the understanding of the evolution of magmatic–hydrothermal systems was recognised in the last few decades, and there are

important contributions from the U–Pb method. Applied primarily on accessory zircon, it was developed further to cover magmatic and hydrothermal accessory and ore minerals and a temperature range from >800 °C to <250 °C (Fig. 1), corresponding to magmatic, hydrothermal and exhumation stages of ore deposits (e.g. Chiaradia, 2013; Chelle-Michou, Schaltegger 2023). There was a revival in the use of the method with the recent development of analytical techniques. Three are the main principal analytical methods used for U–Pb geochronology: Isotope Dilution-Thermal Ionisation Mass Spectrometry (ID-TIMS), Secondary Ion Mass Spectrometry (SIMS), and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). They have their advantages and disadvantages (Table 1), however the high-precision CA-ID-TIMS (“chemical abrasion” ID-TIMS) U–Pb geochronology using parts of single zircon crystals is called “gold standard” of geochronology (Schaltegger et al., 2024) due to its “unprecedented” precision of less than 0.1–0.01%. This is of great importance when the duration of the mineralization processes under study is short, e.g. <25,000 years as defined for the Alumbra porphyry copper deposit in Argentina (Buret et al., 2016).

However, CA-ID-TIMS U–Pb dating is time- and cost-intensive (Table 1) and requires clean labs and high-precision TIMS equipment that is not available in many institutions and countries. Other techniques, such as LA-ICP-MS, are faster, cost-effective, more accessible, easy to use, and have a spatial resolution of several tens of microns (applied in situ with typical ablation craters of 25–50 µm).

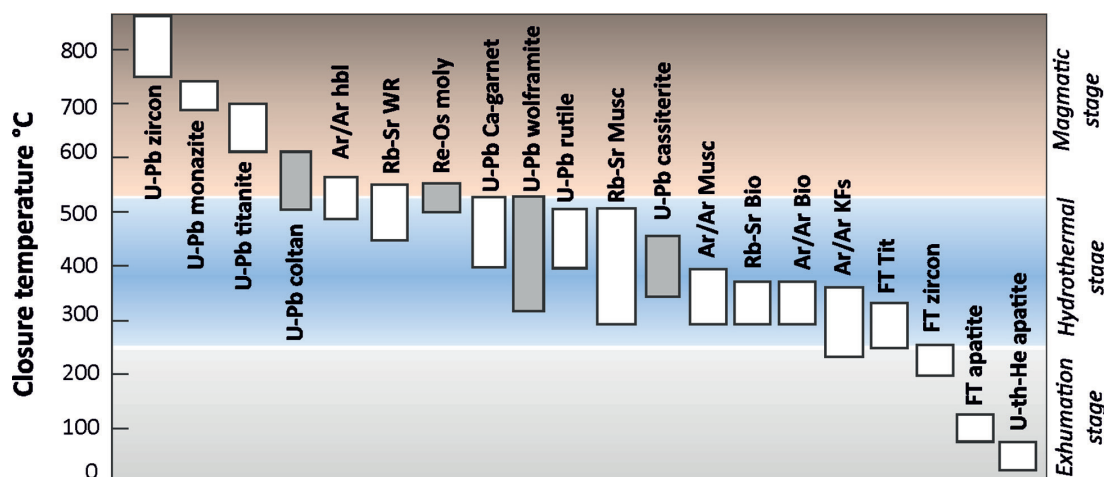


**Fig. 1.** Range of closure temperatures for various geochronometers (modified after Chiaradia et al., 2013) in magmatic–hydrothermal systems and pegmatite deposits. The grey rectangles mark ore minerals used for Nb, Ta, W, Sn extraction and U–Pb dating (columbite–tantalite, wolframite and cassiterite), or Re–Os dating and Mo–Re extraction (molybdenite).

Therefore, depending on the purpose of the study, LA-ICP-MS is preferred in many deposit-focused investigations, including those in Bulgaria. The LA-ICP-MS facilities at the Geological Institute of the Bulgarian Academy of Sciences (GI-BAS) have enabled the joint GI-BAS and Sofia University (Faculty of Geology and Geography, FGG-SU) team to apply U–Pb dating to a wide range of deposit types in Bulgaria. Many of these represent deposits or occurrences of critical and strategic raw materials (CSRMs), including Cu in the porphyry-copper deposits Elatsite and Assarel (with Mo, Re, Sb, Se, Ti, Nb, etc. potential by-products: Peytcheva et al., 2022; Stefanova et al., 2023); W–Bi–Mo and additional metals in intrusion-related gold systems such as Babyak (Stavrev et al., 2020); Be–Nb–Ta–Y in pegmatites (e.g., Peytcheva et al., 2021; Georgieva et al., 2021); and Al with Ti, Ga, and REEs in bauxites (Peytcheva, Hikov, 2025). Considering the chain of processes leading to deposit formation – lithosphere–crust interaction, regional and local tectonics, magmatism, fluid generation and focusing, and metal precipitation (Heinrich, 2024) – the application of LA-ICP-MS U–Pb dating in tectonic and regional-geological studies can significantly improve our understanding of the fertile periods, rock units, and processes responsible for the formation and preservation of CSRM deposits.

The U–Pb method is also applied in fission-track analysis using LA-ICP-MS, a technique for dating of geological processes based on the accumulation of damage trails produced by the spontaneous nuclear fission of  $^{238}\text{U}$  in minerals (mostly apatite and zircon) and glasses. Its application is essential for reconstructing the thermal evolution of rocks and ore deposits at upper-crustal levels, within a temperature range of approximately 60 °C to 300 °C. This approach, in which the  $^{238}\text{U}$  content of minerals is determined directly by LA-ICP-MS, has been successfully implemented over the past two decades (Hasebe et al., 2004).

Last but not least, either simultaneously or subsequent to U–Pb dating, the trace-element composition of minerals such as zircon, apatite, titanite, and rutile can be determined using LA-ICP-MS. These data provide valuable geochemical information for estimating oxidation state, water content, and, more broadly, the sources of elements and the generation and evolution of the studied rocks (Hoskin, Schaltegger, 2003; Dilles et al. 2015; Loucks, Fiorentini, 2023).

### Advances in the U-Pb methods and applications for critical raw material research

The advantages and unique application of the U-Pb CA-ID-TIMS techniques are best demonstrated in porphyry-copper deposits (PCDs), which are characterized by multiple magma emplacement and related hydrothermal veining, alteration and copper deposition. In such systems, high-precision geochronology is essential for bracketing fertile magmatism and mineralization, and can even help in predicting ore grades (e.g., in supergiant PCDs where copper endowment correlates with the timescales of magmatic and hydrothermal activity: Virmond et al., 2024). The technique has been applied to the Elatsite PCD and integrated with other isotopic methods, including low-temperature fission-track (FT) and (U–Th)/He thermochronology. High-precision CA-ID-TIMS U–Pb zircon refined the ages of porphyry and aplitic dykes that bracket the formation of the Elatsite Cu–(Mo–Au) deposit. The main mineralization is confined by individually dated igneous events between  $92.329 \pm 0.021$  Ma and  $92.050 \pm 0.019$  Ma, thus the entire time span of ore-forming magmatism and high-temperature hydrothermal activity extended over a maximum duration of 0.31 Ma, significantly shorter than the previously inferred 1.1 Ma based on conventional ID-TIMS U–Pb zircon dat-

Table 1. Comparison of LA-ICP-MS and CA-ID-TIMS U-Pb dating techniques, using selected criteria

| Criteria                  | LA-ICP-MS                                                                 | CA-ID-TIMS                                                                                 |
|---------------------------|---------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|
| Spatial resolution        | 10–60 microns spot size, 5–20 microns depth                               | Dissolution of a single grain or part of grain                                             |
| Sample preparation        | Zircon mount of 1–10 samples with 20–100 grains; CL-BSE images (2–4 days) | Clean lab; chemical abrasion; dissolution, Pb and U separation (10–15 days for 15 zircons) |
| Time for isotope analyses | 2–3 min, 5–10 min data reduction                                          | 3–4 h; 5–10 min data reduction                                                             |
| Precision and accuracy    | 1–5% precision per analysis (2 sigma); moderate accuracy                  | 0.01–0.3% precision (2 sigma); high accuracy                                               |

ing (Von Quadt et al., 2002). The preservation of the Late Cretaceous Elatsite deposit might be linked to Paleocene–Eocene compression in the Balkan Belt, which caused tectonic burial and protected the system from erosion. During the Late Eocene–Oligocene (U–Th/He apatite ages of  $39.3 \pm 3.0$  Ma), the region cooled below  $\sim 75$  °C and was subsequently exhumed, exposing the 3–4 km-deep porphyry system at the surface (Peytcheva et al., 2017). For the Elatsite and Assarel PCD, as well as for the Chelopech Cu–Au high-sulfidation epithermal deposit, the LA-ICP-MS U–Pb zircon dating was applied prior to the CA-ID-TIMS analyses and helped identify the Late Cretaceous zircon population and establish the general time frame of ore deposition. Although LA-ICP-MS precision was insufficient to resolve the ages of multiple shallow intrusions and dykes within analytical uncertainty, the zircon age data were crucial for selecting the youngest grains for subsequent CA-ID-TIMS analysis (see methodological details in Large et al., 2021; Schaltegger et al., 2024).

Although LA-ICP-MS U–Pb age data are not highly precise, thousands of studies worldwide – and numerous examples from Bulgaria – demonstrate the effectiveness of this technique, especially given its accessibility to the broader Earth science community. Beyond its applications in magmatic–hydrothermal deposits, zircon dating and trace element analysis have proven to be reliable tools for constraining magmatism in the Late Cretaceous Apuseni–Banat–Timok–Srednogorje magmatic belt, a major source of volcanic ash that contributed to the formation of bauxites in Bosnia and Herzegovina (Bilić et al., 2025).

The application of the U–Pb isotope method to grossular-andradite garnets ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ – $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ ), commonly referred to as grandites, has been known for several decades. However, advances in U–Pb geochronology over the past decade (Seman et al., 2017; Salnikova et al., 2019; Waforn et al., 2018) have demonstrated the capacity of Ca-garnets to record hydrothermal processes in ore-forming systems. Importantly, grandite ages have been shown to remain unaffected by subsequent tectonic overprinting (Gevedon et al., 2018; Salnikova et al., 2019). The renewed interest in grandite research across diverse lithologies and skarn deposits reflects not only their utility as reliable geochronometers but also their significant potential for element substitution and trace-element incorporation, including uranium (Antao, 2015; Gevedon et al., 2018; Salnikova et al., 2019). In andradite-rich garnets, the substitution of  $\text{Fe}^{3+}$  for  $\text{Al}^{3+}$  in the octahedral site facilitates the incorporation of large cations (e.g., REEs, Th, U), accompanied by

vacancies to maintain charge balance (DeWolf et al., 1996).

The LA-ICP-MS U–Pb dating technique has been applied to grandites from skarn deposits in Bulgaria and across the Balkan region (Peytcheva et al., 2019; Vassileva et al., 2019a, b). For example, it was used to constrain the timing of skarn formation and associated early hydrothermal mineralization at the Babyak Mo–Ag–Au–W–Bi–base-metal deposit in the Western Rhodopes, Bulgaria, yielding an age of  $68.55 \pm 0.74$  Ma (Stavrev et al., 2019). This direct dating of hydrothermal grandite made it possible to distinguish an early, weakly mineralized Late Cretaceous stage – related to the  $71.12 \pm 0.72$  Ma granodiorites – from a later, ore-bearing Eocene magmatic–hydrothermal stage at approximately 52–54 Ma (Stavrev et al., 2020; Peytcheva et al., 2021).

A potential limitation of LA-ICP-MS U–Pb dating of grandites arises in cases of either elevated Pb concentrations (e.g., in Pb-rich base-metal deposits) or very low U contents. Under such conditions, laser-ablation high-resolution mass spectrometry (LA-HR-ICP-MS) offers distinct advantages over quadrupole ICP-MS (LA-Q-ICP-MS). Both analytical approaches were applied to grandites from the Martinovo Fe(–W–Mo) skarn deposit, part of the Chiprovtsi ore zone in the Western Balkan, Bulgaria. High-resolution LA-HR-ICP-MS U–Pb dating, performed using a Thermo Fisher Element XR coupled to a Resonetics Resolution 155 system at ETH Zurich, yielded an age of  $306.2 \pm 1.9$  Ma, consistent with the ID-TIMS Concordia age of  $306.6 \pm 1.4$  Ma (Vassileva et al., 2020a). The relatively high U contents (10–70 ppm) of these grandites also enabled LA-Q-ICP-MS dating at GI-BAS (Table 2; Fig. 2), producing a lower-intercept age of  $303.7 \pm 5.2$  Ma using the matrix-matched Dashkesan garnet external standard reference material (Stifeeva et al., 2018), and  $317.8 \pm 9.0$  Ma when employing the GJ-1 zircon standard. These results overlap within analytical uncertainty with the ID-TIMS age. Collectively, the age data support a possible genetic link to the Sveti Nikola granite ( $313.8 \pm 3.5$  Ma; Carrigan et al., 2005) or related granitoid intrusions.

The LA-Q-ICP-MS U–Pb columbite–tantalite dating technique was applied to constrain the age of the Vishteritsa pegmatite (Western Rhodopes), using the X36 matrix-matched standard reference material (SRM) (von Quadt et al., 2019; Peytcheva et al., 2021). This approach was subsequently employed for dating Variscan pegmatites in Slovakia (Uher et al., 2024). Titanites from pegmatites in the Madan region have also been successfully dated, providing important insights into the succession of magmatic and hydrothermal processes (Georgieva et al., 2022).

Table 2. LA-Q-ICP-MS U-Pb isotope data for Ca-garnets of Martinovo Fe(-W-Mo) skarn deposit, Western Balkan, Bulgaria

| Name                                            | Source file | $^{207}\text{Pb}/^{235}\text{U}$<br>ratio | Int<br>2SE | $^{206}\text{Pb}/^{238}\text{U}$<br>ratio | Int<br>2SE | Error<br>Corr | $^{207}\text{Pb}/^{206}\text{Pb}$<br>ratio | Int<br>2SE | $^{207}\text{Pb}/^{235}\text{U}$<br>age, Ma | Int<br>2SE | $^{206}\text{Pb}/^{238}\text{U}$<br>age, Ma | Int<br>2SE |
|-------------------------------------------------|-------------|-------------------------------------------|------------|-------------------------------------------|------------|---------------|--------------------------------------------|------------|---------------------------------------------|------------|---------------------------------------------|------------|
| <i>Dashkesan granulite primary SRM (GI-BAS)</i> |             |                                           |            |                                           |            |               |                                            |            |                                             |            |                                             |            |
| CHI1Sof_1                                       | 18sp28c09   | 0.300                                     | 0.220      | 0.0479                                    | 0.0073     | 0.113         | 0.037                                      | 0.024      | 70                                          | 150        | 299                                         | 45         |
| CHI1Sof_2                                       | 18sp28c10   | 0.223                                     | 0.086      | 0.0482                                    | 0.0040     | 0.012         | 0.015                                      | 0.007      | 159                                         | 66         | 302                                         | 25         |
| CHI1Sof_3                                       | 18sp28c11   | 0.340                                     | 0.230      | 0.0503                                    | 0.0087     | 0.217         | 0.051                                      | 0.028      | 130                                         | 160        | 324                                         | 56         |
| CHI1Sof_4                                       | 18sp28c12   | 0.280                                     | 0.150      | 0.0483                                    | 0.0058     | 0.328         | 0.010                                      | 0.009      | 160                                         | 110        | 302                                         | 35         |
| CHI1Sof_5                                       | 18sp28c13   | 0.264                                     | 0.058      | 0.0481                                    | 0.0029     | 0.082         | 0.014                                      | 0.003      | 215                                         | 44         | 302                                         | 18         |
| CHI1Sof_6                                       | 18sp28c14   | 0.238                                     | 0.086      | 0.0476                                    | 0.0043     | 0.011         | 0.014                                      | 0.006      | 180                                         | 67         | 299                                         | 26         |
| CHI1Sof_7                                       | 18sp28c15   | 0.329                                     | 0.076      | 0.0515                                    | 0.0035     | 0.035         | 0.016                                      | 0.004      | 266                                         | 58         | 323                                         | 22         |
| CHI1Sof_8                                       | 18sp28c16   | 0.340                                     | 0.120      | 0.0509                                    | 0.0047     | 0.146         | 0.017                                      | 0.007      | 248                                         | 91         | 319                                         | 28         |
| CHI1Sof_9                                       | 18sp28c17   | 0.288                                     | 0.066      | 0.0495                                    | 0.0036     | 0.014         | 0.014                                      | 0.003      | 242                                         | 53         | 311                                         | 22         |
| CHI1Sof_10                                      | 18sp28c18   | 0.320                                     | 0.070      | 0.0490                                    | 0.0028     | 0.009         | 0.014                                      | 0.003      | 260                                         | 53         | 308                                         | 17         |
| CHI1Sof_11                                      | 18sp28c19   | 0.308                                     | 0.067      | 0.0491                                    | 0.0035     | 0.045         | 0.013                                      | 0.003      | 262                                         | 55         | 309                                         | 22         |
| CHI1Sof_12                                      | 18sp28c20   | 0.332                                     | 0.062      | 0.0488                                    | 0.0026     | 0.077         | 0.013                                      | 0.002      | 266                                         | 46         | 307                                         | 16         |
| <i>GJ1 zircon primary SRM (GI-BAS)</i>          |             |                                           |            |                                           |            |               |                                            |            |                                             |            |                                             |            |
| CHI1Sof_1                                       | 18sp28c09   | 0.53                                      | 0.39       | 0.0537                                    | 0.0082     | 0.113         | 0.145                                      | 0.095      | -80                                         | 240        | 333                                         | 50         |
| CHI1Sof_2                                       | 18sp28c10   | 0.39                                      | 0.15       | 0.0535                                    | 0.0045     | 0.012         | 0.058                                      | 0.027      | 230                                         | 100        | 335                                         | 27         |
| CHI1Sof_3                                       | 18sp28c11   | 0.57                                      | 0.38       | 0.055                                     | 0.0095     | 0.218         | 0.21                                       | 0.12       | 70                                          | 240        | 353                                         | 61         |
| CHI1Sof_4                                       | 18sp28c12   | 0.45                                      | 0.25       | 0.0524                                    | 0.0063     | 0.327         | 0.044                                      | 0.038      | 180                                         | 160        | 327                                         | 38         |
| CHI1Sof_5                                       | 18sp28c13   | 0.42                                      | 0.09       | 0.0518                                    | 0.0031     | 0.083         | 0.061                                      | 0.013      | 310                                         | 62         | 325                                         | 19         |
| CHI1Sof_6                                       | 18sp28c14   | 0.37                                      | 0.13       | 0.0509                                    | 0.0046     | 0.011         | 0.064                                      | 0.025      | 247                                         | 93         | 319                                         | 28         |
| CHI1Sof_7                                       | 18sp28c15   | 0.47                                      | 0.11       | 0.0557                                    | 0.0038     | 0.006         | 0.073                                      | 0.019      | 349                                         | 79         | 349                                         | 23         |
| CHI1Sof_8                                       | 18sp28c16   | 0.50                                      | 0.18       | 0.0535                                    | 0.0049     | 0.015         | 0.078                                      | 0.032      | 320                                         | 120        | 335                                         | 30         |
| CHI1Sof_9                                       | 18sp28c17   | 0.41                                      | 0.09       | 0.0517                                    | 0.0037     | 0.014         | 0.068                                      | 0.016      | 318                                         | 69         | 324                                         | 23         |
| CHI1Sof_10                                      | 18sp28c18   | 0.44                                      | 0.09       | 0.0504                                    | 0.0029     | 0.008         | 0.071                                      | 0.016      | 329                                         | 66         | 316                                         | 18         |
| CHI1Sof_11                                      | 18sp28c19   | 0.41                                      | 0.09       | 0.0501                                    | 0.0036     | 0.046         | 0.068                                      | 0.015      | 328                                         | 67         | 315                                         | 22         |
| CHI1Sof_12                                      | 18sp28c20   | 0.43                                      | 0.08       | 0.0494                                    | 0.0027     | 0.075         | 0.065                                      | 0.012      | 325                                         | 56         | 310                                         | 16         |

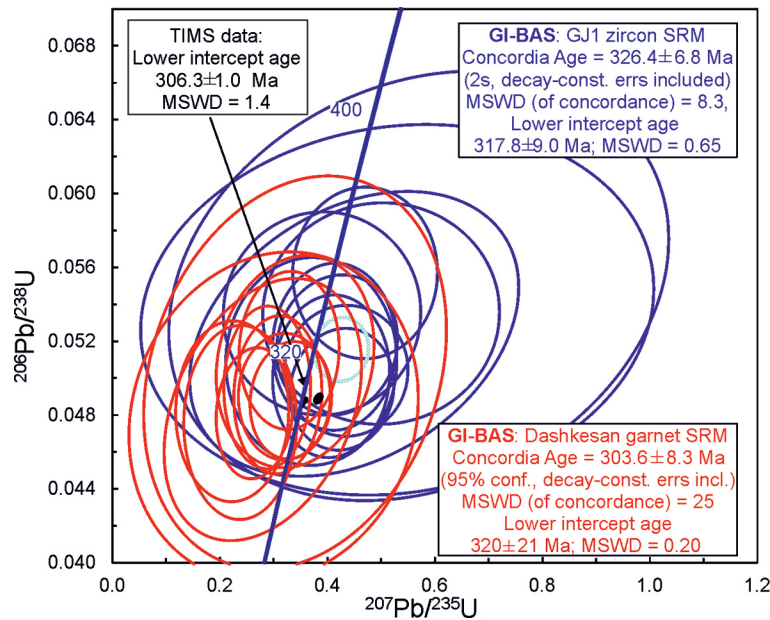


**Fig. 2.** U-Pb Concordia diagram for Ca-garnets of Martinovo Fe(-W-Mo) skarn deposit, Chiprovtsi ore zone, Western Balkan, Bulgaria. The results of the LA-Q-ICP-MS U-Pb dating results (analytical conditions: 50 microns LA crater, 8 Hz repetition rate), applying Dashkesan garnet and GJ-1 zircon SRMs, are compared with the most precise ID-TIMS age of the garnets.

LA-Q-ICP-MS U–Pb dating of wolframite from the Polski Gradets deposit was conducted in the GI-BAS laboratory on two samples, yielding an intercept age of  $78 \pm 13$  Ma (MSWD = 0.2) and a  $^{206}\text{Pb}/^{238}\text{U}$  mean age of  $76.5 \pm 6.8$  Ma (95% confidence, MSWD = 0.20) using GJ-1 zircon as the primary standard reference material (SRM). When wolframite YGX2113 was employed as the primary SRM, the resulting  $^{206}\text{Pb}/^{238}\text{U}$  mean age was  $79.0 \pm 6.8$  Ma (95% confidence, MSWD = 0.079; Peytcheva et al., 2024). The technique has recently been applied to wolframite from >1000 Ma tungsten deposits in Colombia, as well as to cassiterite and wolframite from a Variscan deposit in Poland.

With a combination of U–Pb age data it was possible to restore the succession of processes that resulted in the formation of Li-bearing pegmatites in southern Zambia. The LA-Q-ICP-MS U–Pb dating was applied to zircon, monazite and columbite–tantalite (coltan) from Mapatizya granites and lithium pegmatite dykes, intruding the metasedimentary basement of the Paleo– to Mesoproterozoic Choma–Kalomo Block. The zircons are metamict and predominantly discordant, with only two grains yielding (sub)concordant ages of  $1189 \pm 37$  Ma ( $2\sigma$ ). The monazites from the granite are mostly concordant, ranging from  $1169 \pm 14$  Ma to  $1302 \pm 44$  Ma, with a principal cluster at  $1205 \pm 15$  Ma. Age determinations for columbite–tantalite from the MLP are largely concordant, with a few subconcordant analyses. The main population yields ages between  $1126 \pm 16$  Ma and  $1060 \pm 15$  Ma, defining a Concordia age of  $1080.4 \pm 5.0$  Ma, while the second group gives an age of  $1001 \pm 9$  Ma. These results indicate that the pegmatites formed between >1080 Ma and <1200 Ma, and that the columbite–tantalite experienced partial resetting during a tectono-metamorphic event around 950–1000 Ma.

In Bulgaria, fission-track analysis using the LA-ICP-MS U–Pb method was applied for the first time to reconstruct the Alpine thermal and tectonic evolution of the central part of the Sredna Gora Zone (Balkanska et al., 2022). The post-magmatic, metallogenic, and tectonic evolution of the rocks from the Chelopech Au–Cu deposit was constrained accordingly, providing key insights into the processes responsible for the accommodation, preservation, and subsequent erosion of the ore system. (Balkanska et al., 2023).

## Conclusions

The combined use of U–Pb isotope dating and trace-element geochemistry of accessory and ore minerals represents a powerful approach for inves-

tigating CSRM deposits and occurrences. The LA-ICP-MS facility at GI-BAS has been developed to enable U–Pb dating of zircon, monazite, titanite, columbite–tantalite, wolframite, cassiterite, apatite, Ca-garnets, and rutile, and has been successfully applied to a wide range of deposit types – including magmatic-hydrothermal systems, pegmatites, and bauxites – in Bulgaria, Europe, and beyond. Further methodological advances are anticipated with the newly acquired LA-ICP-MS/MS (QQQ) system at GI-BAS, comprising an Agilent 8900 Triple Quadrupole ICP-MS/MS and an Elemental Scientific ImageGEO193 automated laser system equipped with the Mlase MLI-1000-LC excimer laser. This instrumentation will facilitate integrated U–Pb geochronology and mineral-tracing studies alongside additional isotope systems such as Lu–Hf (in garnet and zircon), Re–Os (in molybdenite), and Rb–Sr (in muscovite, biotite, and lepidolite), thereby enhancing our understanding of the geological processes responsible for the formation of CSRM deposits.

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