中国科学: 地球科学 2021 年 第 51 卷 第 1 期: 171 ~ 174
SCIENTIA SINICA Terrae earthcn.scichina.com
《中国科学》杂志社 SCIENCE CHINA PRESS

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黑钨矿微区原位U-Pb年代学方法及应用

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收稿日期: 2020-04-23; 收修改稿日期: 2020-08-07; 接受日期: 2020-09-02; 网络版发表日期: 2020-10-16
国家自然科学基金项目(批准号: 41525012)资助

钨(W)是重要的关键性金属资源之一, 广泛用于电子、石油、化工及军事工业等领域. 中国钨矿资源丰富(储量占全球~60%, 年产量占全球~80%), 是世界上重要的钨金属资源基地, 其中华南地区(赣南-粤北-湘南)是中国钨矿成矿带重要产区. 充分了解其矿床成因、精细成矿过程和矿床分布规律, 将进一步指导矿床的寻找和勘查. 成矿时代是解决上述问题的基础, 也是矿床学研究中的难点与热点. 由于钨矿通常与锡矿和花岗岩伴生或共生, 人们通常采用花岗岩中锆石和矿体中脉石矿物(如云母、长石等)或与其伴生的辉钼矿来间接限定钨矿成矿时代, 但W作为金属元素, 其富集和成矿的物理化学条件与硅酸盐中造岩元素和Mo等其他金属元素具有显著差异, 所获得的年龄结果难以有效制约钨矿的真正形成年龄. 黑钨矿(钨锰铁矿, $(Fe,Mn)WO_4$)是钨的主要赋存矿物, 也是提炼钨的最主要矿石, 如果能够直接对矿石矿物——黑钨矿开展年代学研究, 则无疑可以给出更可靠的钨矿成矿年代.

尽管20世纪80年代初研究就已表明, 黑钨矿通常含有一定U, 是U-Pb定年的潜在对象, 但是黑钨矿U-Pb年代学方法研发进展缓慢. 率先成功获得有意义黑钨矿U-Pb年龄的是德国波茨坦地球科学研究中心(GFZ)的Rolf L. Romer教授团队, 他们对美国科罗拉多Sweet Home Mine黑钨矿开展了同位素稀释法热电离质谱(ID-TIMS)U-Pb年代学工作, 获得黑钨矿$^{206}Pb/^{238}U$年龄为(25.7±0.3)Ma(Romer和Lüders, 2006). 随后, 他们对德国Clara Mine(Pfaff等, 2009)、法国中央陆块(Harlaux等, 2018a)以及中国广西五通(Lecumberri-Sanchez等, 2014)和江西荡坪(Legros等, 2020)产出的黑钨矿进行了ID-TIMS U-Pb定年工作, 直接限定了钨矿的成矿时代. 目前, 所有黑钨矿ID-TIMS U-Pb年代学工作都是在GFZ实验室完成的. 但黑钨矿中通常含有大量高普通铅矿物(如白钨矿、方铅矿、闪锌矿和硫化物等)包裹体, ID-TIMS方法需要全部溶解黑钨矿颗粒, 很难避开上述矿物的干扰与影响, 成功率往往并不高, 限制了黑钨矿ID-TIMS U-Pb年代学方法的广泛使用和推广(Romer和Lüders, 2006; Pfaff等, 2009; Lecumberri-Sanchez等, 2014; Harlaux等, 2018a; Legros, 2017; Legros等, 2020).

开展黑钨矿微区原位U-Pb年龄测定无疑是解决这个难题的有效途径. 最近, 中国地质大学(武汉)和中国科学院地球化学研究所研究团队先后报道了激光微区原位等离子质谱(LA-ICP-MS)黑钨矿U-Pb年龄测定的分析方法.

中文引用格式: 杨岳衡, 杨明, 王浩, 杨进辉, 吴福元. 2021. 黑钨矿微区原位U-Pb年代学方法及应用. 中国科学: 地球科学, 51(1): 171–174, doi: 10.1360/SSTe-2020-0107
英文引用格式: Yang Y, Yang M, Wang H, Yang J, Wu F. 2021. Methodology for *in situ* wolframite U-Pb dating and its application. Science China Earth Sciences, 64 (1): 187–190, https://doi.org/10.1007/s11430-020-9676-3

中国地质大学(武汉)团队采用的是锆石外标水蒸气辅助法(Luo等, 2018, 2019). 他们系统地研究了水蒸汽、氧气和氮气对激光剥蚀等离子质谱测定矿物U-Pb年龄的影响. 在激光剥蚀的气溶胶中混入少量水蒸汽, 显著降低了不同矿物之间在激光剥蚀过程中产生的U/Pb分馏差异, 从而建立了以锆石/NIST610玻璃为外标, 获得独居石、磷钇矿、榍石和黑钨矿U-Pb年龄的方法. 他们对来自法国中央地块中的LB和MTM黑钨矿样品进行了测定, 获得与ID-TIMS U-Pb年龄((333.4±2.4)Ma和(334.4±1.7)Ma)在误差范围内一致的年龄结果, 验证了该方法的可行性. 随后, 他们对中国湖南瑶岗仙和江西漂塘产出的黑钨矿开展了应用研究, 分别获得了(159.1±2.0)Ma(n=12, MSWD=0.5)和(153.7±0.7)Ma(n=26, MSWD=0.7), (159.5±1.3)Ma(n=14, MSWD=0.3)和(152.1±0.9)Ma(n=22, MSWD=0.5)的两期黑钨矿U-Pb年龄, 这些结果也得到了相关岩相学证据的支持(Deng等, 2019). 同时, 这些黑钨矿U-Pb年龄明显不同于以前云母Rb-Sr和热液锆石U-Pb法给出的年龄(134Ma), 虽然辉钼矿Re-Os等时线定年给出了与黑钨矿U-Pb年龄大体一致的结果(170~150Ma), 但是其较大的年龄范围和误差表明, 辉钼矿Re-Os体系可能存在放射性母子体的解耦或/和多时代矿物的混合, 不能代表真实的钨矿成矿时代, 这更加突显矿石矿物——黑钨矿微区原位U-Pb年代学的优势.

中国科学院地球化学研究所团队采用的是NIST玻璃和黑钨矿MTM联合校正法(Tang等, 2020). 他们发现, MTM颗粒间U含量非常不均一, 且含有相当量的普通铅, 不适合作为黑钨矿微区U-Pb定年标样. 因此, 作者使用NIST612或614与MTM分别来校正实际样品$^{207}Pb/^{206}Pb$和$^{238}U/^{206}Pb$比值, 然后构建Tera-Wasserburg图解, 获得其下交点$^{206}Pb/^{238}U$年龄, 并以中国江西西华山与漂塘、浙江朗村、内蒙古沙麦和新疆白干湖钨锡矿田产出的黑钨矿为应用实例进行方法有效性检验. 西华山黑钨矿给出的U-Pb年龄为(160.9±1.9)Ma(n=19, MSWD=1.0), 与辉钼矿、独居石与磷钇矿的年龄基本一致. 漂塘黑钨矿的U-Pb年龄为(153.6±1.4)Ma(n=28, MSWD=2.0), 与利用锆石外标水蒸气辅助法所获年龄(~153Ma)一致. 朗村黑钨矿U-Pb年龄为(127.4±4.8)Ma(n=30, MSWD=1.8), 与花岗岩中锆石所给出的一组较年轻的年龄((131.2±1.8)Ma, n=5, MSWD=0.7)基本一致, 小于锆石给出的另一组(144.6±1.2)Ma(n=19, MSWD=0.8)的年龄. 沙麦黑钨矿U-Pb年龄为(142.3±1.3)Ma(n=34, MSWD=1.8), 与白云母Ar-Ar年龄(140±1)Ma一致. 白干湖黑钨矿U-Pb年龄为(425.9±4.3)Ma(n=19, MSWD=1.0)和(429.2±6.8)Ma(n=23, MSWD=2.0), 与锡石记录的年龄((427.6±5.1)Ma, n=29, MSWD=2.4)一致. 上述结果显示了该方法的可靠性和广泛适用性.

这些创新性方法极大降低了激光微区原位U-Pb年龄测定对同种矿物标样的依赖, 拓宽了激光微区矿物U-Pb年代学方法的应用范围, 显示出黑钨矿微区原位U-Pb方法的明显优势与广阔应用前景. 但是, 黑钨矿微区原位U-Pb年代学方法目前仍处于起步阶段, 与常见微区原位U-Pb定年矿物(锆石, 榍石, 独居石等)不同, 黑钨矿U含量通常比较低, 而且变化范围非常大, 不同地区或者同一矿区产出黑钨矿U含量变化范围为2~4个数量级(<0.1ppm U或>100ppm U, 1ppm=1×10^{-6})(图1和2), 同时, 黑钨矿通常含有一定的普通铅, 且普通铅含量变化范围也非常大(<10%或>90%)(图2b). 黑钨矿U-Pb标准物质缺乏, 目前还没有国际通用的标准. 这些特征, 无疑给黑钨矿进一步微区原位U-Pb年代学研究和应用带来困难与挑战.

未来微区原位黑钨矿U-Pb年代学方法及应用研究可能要注意以下几个方面: (1) 黑钨矿微区原位U-Pb年龄标样的研发. 进一步寻找相对均一、较高U含量且低普通Pb含量的黑钨矿U-Pb年龄标样, 这需要国内外同行的长期努力与协作. 目前只有德国GFZ实验室可以开展黑钨矿ID-TIMS U-Pb年代学工作. 中国还没有相关实验室能够进行这方面的工作. 同样, 绝大部分其他副矿物U-Pb的ID-TIMS U-Pb定年工作也都需在国外实验室完成, 国内亟待加强这方面的工作(王伟等, 2020), 此外, 人工合成黑钨矿标样也是努力的方向. (2) 钨氧化物对Hg和Pb的干扰问题, 如$^{186}W^{16}O$和$^{184}W^{18}O$干扰^{202}Hg, $^{186}W^{18}O$干扰^{204}Hg和^{204}Pb, 钨氧化物对Hg和Pb的干扰, 导致无论是离子探针还是激光探针, 微区原位黑钨矿U-Pb定年都无法进行^{204}Pb校正. 尤其是离子探针U-Pb定年, 采用氧源作为一次离子源会产生大量钨氧化物离子团, 这可能也是迟迟没有黑钨矿离子探针U-Pb年龄报道的主要原因. 已有激光数据表明, 黑钨矿Th/U为10^{0}~10^{-3}(图2a), 比锡石和金红石的Th/U(10^{-4}~10^{-5})高2~4个数量

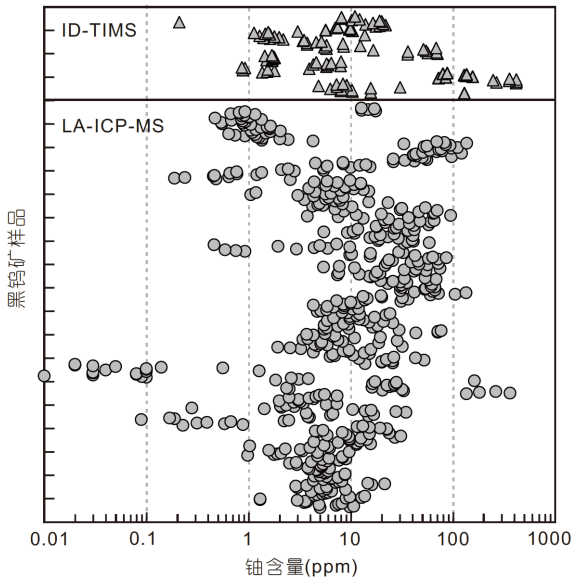

图 1　黑钨矿U含量变化范围

ID-TIMS数据来自Romer和Lüders(2006)、Pfaff等(2009)、Lecumberri-Sanchez等(2014)、Harlaux等(2018a)、Legros等(2017, 2020); LA-ICP-MS数据来自Harlaux等(2018b)、Zhang等(2018)、Deng等(2019)、Luo等(2019)、Legros等(2020)和Tang等(2020)

级, 表明^{208}Pb校正也不适合微区原位黑钨矿U-Pb年龄的测定. 因此, 对于含有普通铅的黑钨矿U-Pb定年, 通过构建Tera-Wasserburg图解, 直接获得下交点年龄是比较可行的方案, 同时低普通铅的样品可以采用^{207}Pb校正, 获得其^{206}Pb/^{238}U年龄. (3) 黑钨矿U-Pb封闭温度. 目前这方面的研究还未见报道. (4) 基体效应. 黑钨矿是钨锰矿和钨铁矿任意比例固溶体, 激光探针与离子探针U-Pb测定钨锰矿与钨铁矿是否存在基体效应未见报道. 相对激光探针而言, 离子探针基体效应尤为敏感, 亟待开展此方面的研究. (5) 黑钨矿一般形成于中温到低温的热液矿床中, 易受热液流体影响而发生蚀变(如白钨矿化等), 因此开展U-Pb定年之前需要进行黑钨矿成矿期次与阶段的甄别与确认; 而黑钨矿的背散射和阴极发光图像易受铁元素的抑制作用, 很难区分不同期次和阶段, 因此, 详实的岩相学准备工作(如能谱和电子探针分析等)是微区原位黑钨矿U-Pb年龄合理解读必不可少的环节(Romer和Lüders, 2006; Pfaff等, 2009; Lecumberri-Sanchez等, 2014; Harlaux等, 2018a; Legros等, 2017, 2020; Deng等, 2019; Tang等, 2020).

总之, 随着微区原位黑钨矿U-Pb年代学方法的不断成熟和日趋完善, 相关技术难题正在得到解决, 显示该方法广泛的应用与推广前景. 随着战略性关键金属成为国内外成矿作用研究新的热点, 黑钨矿、锡石、铌钽矿、氟碳铈矿、独居石等稀有稀土金属矿物微区原位U-Pb年代学方法, 必将为中国新一轮矿床学研究做出应有的学术贡献.

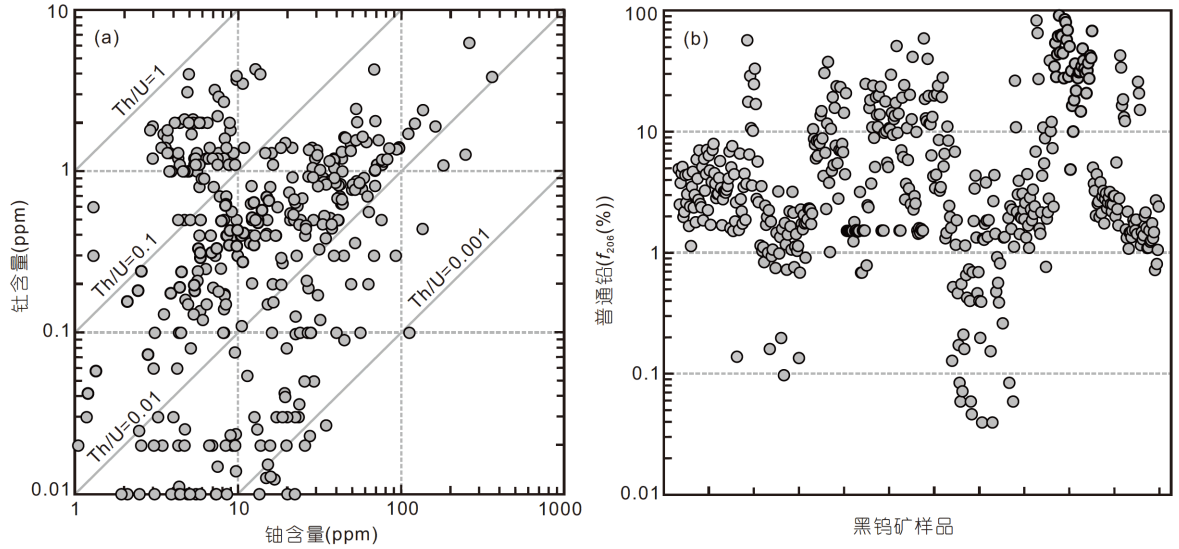

图 2　激光微区原位获得的黑钨矿U、Th含量、Th/U比值和普通铅的变化范围

数据来自Harlaux等(2018b)、Zhang等(2018)、Deng等(2019)、Luo等(2019)、Legros等(2020)和Tang等(2020)

致谢 感谢主编郑永飞老师的邀请和审稿人对本文提出宝贵意见和建议.

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(责任编委: 吴元保)

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January 2021 Vol.64 No.1: 187–190
https://doi.org/10.1007/s11430-020-9676-3

Methodology for *in situ* wolframite U-Pb dating and its application

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Received April 23, 2020; revised August 7, 2020; accepted September 2, 2020; published online October 16, 2020

Citation: Yang Y, Yang M, Wang H, Yang J, Wu F. 2021. Methodology for *in situ* wolframite U-Pb dating and its application. Science China Earth Sciences, 64 (1): 187–190, https://doi.org/10.1007/s11430-020-9676-3

Tungsten (or wolfram, W), one of the crucial metal sources, is widely used in electronics, oil, chemical and military industries. China owns abundant tungsten resources (~60% of the world reserves and ~80% of the world's production), of which the area from Southern Jiangxi-Northern Guangdong-Southern Hunan is the most significant ore belt in south China. Understanding ore genesis and distribution as well as the process of fine mineralization will further benefit the prospecting and exploration of tungsten deposits. The accurate determination of the age of mineralization is at the front line in the study of ore deposit and the premise for solving and understanding the above problems. Tungsten is associated with tin ore and granitic rocks, hence, zircon in granite and the gauge minerals (e.g., mica, feldspar) or the associated molybdenite are usually used to indirectly date and define the time of tungsten mineralization. However, the physical and chemical conditions of tungsten enrichment and ore-forming processes are significantly different from the rock-forming elements and Molybdenum (Mo) and other metals in silicate. Therefore, the obtained age data might not be able to effectively restrict the time of tungsten mineralization. Wolframite [(Fe, Mn)WO_4] is the main ore mineral for tungsten, and also the main ore used to refine tungsten. If the age of ore mineral (wolframite) can be dated and measured *in situ*, we could get a more reliable age of tungsten mineralization.

Previous studies in the early 1980s showed that wolframite usually contains a certain amount of U, suggesting that the mineral could be a good candidate for U-Pb dating. However, a conventional methodology for wolframite U-Pb dating has not yet been established. Romer and Lüders, (2006) from the Potsdam Centre for Geoscience Research (GFZ) in Germany, successfully dated wolframite from the Sweet Home Mine (Colorado, USA) by U-Pb isotope dilution thermal ionization mass spectrometry (ID-TIMS). The $^{206}Pb/^{238}U$ ID-TMS age from the Sweet Home Mine wolframite crystal was 25.7±0.3 Ma (Romer and Lüders, 2006). Later, the same group conducted several ID-TIMS U-Pb dating on wolframite samples from the Clara Mine (Germany; Pfaff et al., 2009), the French Central Massif (France; Harlaux et al., 2018a), the Wutong deposit (Guangxi province, China; Lecumberri-Sanchez et al., 2014) and the Dangping deposit (Jiangxi province, China; Legros et al., 2020), respectively. In order to carry out ID-TIMS, researchers need to dissolve bulk wolframite samples. Since wolframite generally contains a large amount of common Pb-rich mineral inclusions (such as scheelite, galena, sphalerite and sulfides), it is very difficult or impossible to avoid the interference of the mineral inclusions. Therefore, this bulk analysis method might not be working effectively as expected, which hampers the widespread use of wolframite ID-TIMS U-Pb dating technique (Romer and Lüders, 2006; Pfaff et al., 2009; Lecumberri-Sanchez et al., 2014; Harlaux et al., 2018a; Legros, 2017; Legros et al., 2020).

In situ wolframite U-Pb dating is an alternative to solve the above-mentioned problems. Recently, two research groups

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from Wuhan (China University of Geosciences) and the Institute of Geochemistry, Chinese Academy of Sciences, successfully developed and reported wolframite U-Pb dating methodology using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

The research group from Wuhan first used the water vapor-assisted method with zircon as an external standard (Luo et al., 2018, 2019). They systematically investigated the effects of water vapor, oxygen and nitrogen on the U-Pb ages of various minerals during LA-ICP-MS procedure. A small amount of water vapor was mixed into the ablated aerosol, which significantly reduced the U/Pb fractionation difference between various minerals during laser sampling. Their established U-Pb dating protocol was applied to monazite, xenotime, titanite and wolframite dating using zircon or NIST610 as external standard. The yielded ages from wolframite samples LB and MTM from the French Central Massif are consistent with the ID-TIMS U-Pb results of 333.4±2.4 and 334.4±1.7 Ma (Harlaux et al., 2018a), which indicates the feasibility of the protocol. In addition, they carried out a protocol for U-Pb dating of wolframite from the Yaogangxian deposit in Hunan Province and Piaotang deposit in Jiangxi Province, respectively. From both deposits they obtained U-Pb ages of 159.1±2.0 Ma (n=12, MSWD=0.5) and 153.7±0.7 Ma (n=26 MSWD=0.7), 159.5 ±1.3 Ma (n=14, MSWD=0.3) and 152.1±0.9 Ma (n=22, MSWD=0.5), which were verified by related petrographic evidences (Deng et al., 2019). Meanwhile, the U-Pb ages of wolframite samples are obviously different from the ca. 134 Ma reported mica Rb-Sr isochron and hydrothermal zircon U-Pb ages. Although the molybdenite Re-Os isochron age (170–150 Ma) is generally similar to the wolframite U-Pb ages, the larger age range and error illustrate that the molybdenite Re-Os system may be characterized by the decoupling of the radioactive parent and daughter isotopes or the mixing of multiage minerals, and cannot represent the true tungsten mineralization age. This highlights the advantage of *in situ* wolframite U-Pb chronology over bulk analysis.

The second research group from the Institute of Geochemistry, Chinese Academy of Sciences adopted a combined NIST glass and wolframite MTM sample correction method (Tang et al., 2020, references therein). They found that the U and Pb contents of the MTM wolframite are rather heterogeneous and may not be suitable as a primary reference material during *in situ* U-Pb analysis. Consequently, they used NIST612/614 and MTM in combination to correct the $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ ratios of the dated samples, then plotted the data in a Tera-Wasserburg diagram and calculated the lower intercept $^{238}U/^{206}Pb$ age. The feasibility of the method was validated by applying it to several wolframite samples from Xihuashan (Jiangxi Province), Piaotang (Jiangxi Province), Langcun (Zhejiang Province), Shamai (Inner Mongolia) and Baiganhu (Xinjiang) deposit in China. Wolframite from Xihuashan deposit yielded an age of 160.9±1.9 Ma (n=19, MSWD=1.0) which is in good agreement with molybdenite, monazite and xenotime ages. The U-Pb age from Piaotang is 153.6±1.4 Ma (n=28, MSWD=2.0); this result is in good agreement with the wolframite U-Pb age (~153 Ma) obtained by the water vapor-assisted method with zircon as an external standard. The Langcun wolframite yielded a U-Pb age of 127.4±4.8 Ma (n=30, MSWD=1.8) which is very close to the younger group age of 131.2±1.8 Ma (n=5, MSWD=0.7) from the zircon in granite, but clearly younger than the older zircon group age of 144.60±1.2 Ma (n=19, MSWD=0.8). The U-Pb age of Shamai wolframite is 142.3±1.3 Ma (n=34, MSWD=1.8), consistent with the muscovite Ar-Ar age (140±1 Ma). Wolframite from Baiganhu deposit yielded the ages of 425.9±4.3 Ma (n=19, MSWD=1.0) and 429.2±6.8 Ma (n=23, MSWD=2.0), which are in good agreement with the cassiterite age (427.6±5.1 Ma, n=29, MSWD=2.4; Tang et al., 2020). The above results exemplify the accuracy and widespread applicability of their method.

These innovative methods greatly undermined the dependence of *in situ* U-Pb dating on the same type mineral reference material, which broadened the application of *in situ* laser ablation U-Pb chronology, and exhibited the obvious advantages and wide application prospects of *in situ* wolframite U-Pb dating. However, the U content in wolframite is often relatively low and with huge variations in different regions or in the same mining area, ranging from 2 to 4 magnitude (from lower than 0.1 ppm to higher than 100 ppm, 1ppm=1×10^{-6}; Figures 1 and 2). This characteristic is different from other common dating minerals (zircon, titanite, monazite, etc.). In addition, wolframite contains a certain amount of common Pb which also varies widely (from lower than 10% to higher than 90%; Figure 2b). On the other hand, there is no international wolframite U-Pb standard available. These obstacles bring difficulties and challenges to the application of *in situ* U-Pb chronology.

The following aspects should be taken into account in the future for *in situ* U-Pb dating of wolframite: (1) Reference materials development for *in situ* U-Pb dating of wolframite: in order to further establish relatively uniform and high U content along with low common Pb composition reference materials for wolframite U-Pb dating, it is required the long-term efforts and cooperation of domestic and foreign counterparts. At present, the ID-TIMS U-Pb dating of wolframite is only done at GFZ in Germany, and there is no reported ID-TIMS U-Pb work of wolframite in China to our knowledge. Coincidentally, the ID-TIMS U-Pb dating of most other accessory minerals also needs to be measured in foreign laboratories, therefore it is urgent to strengthen this method in China (Wang et al., 2020). In addition, the synthetic wolframite reference is also a viable plan. (2) The isobaric in-

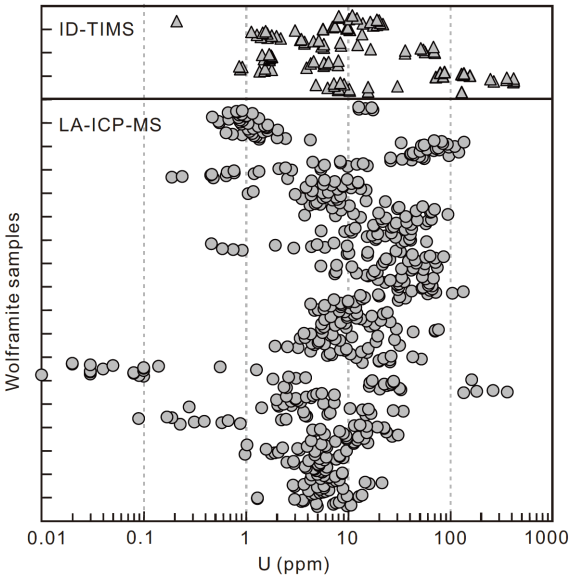

Figure 1 The variation of wolframite U content (ID-TIMS data come from Romer and Lüders, 2006; Pfaff et al., 2009; Lecumberri-Sanchez et al., 2014; Harlaux et al., 2018a; Legros, 2017, Legors et al.,2020; LA-ICP-MS data come from Harlaux et al., 2018b; Zhang et al., 2018; Deng et al., 2019; Luo et al., 2019; Legros et al., 2020; Tang et al., 2020).

terference of tungsten oxides ($^{186}W^{16}O$ and $^{184}W^{18}O$ on ^{202}Hg; $^{186}W^{18}O$ on ^{204}Hg and ^{204}Pb) on Hg and Pb: The interference of tungsten oxides on Hg and Pb leads to no workable approach to perform ^{204}Pb correction for *in situ* wolframite U-Pb dating, no matter the ion probe or the laser probe. Especially, the ion probe U-Pb analysis takes oxygen source as the primary ion source and will produce a large number of tungsten oxides, which may also be the main reason for the non-reported wolframite U-Pb dating research by ion probe. The reported laser data have shown that the Th/U ratio of wolframite is 10^{0}–10^{-3} (Figure 2a), which is 2 to 4 orders of magnitude higher than that of cassiterite and rutile (10^{-4}–10^{-5}). This also indicates that the ^{208}Pb correction method may not be effective for *in situ* wolframite U-Pb dating. In consequence, the best age estimate can be obtained from the intercept age in the Tera-Wasserburg diagram for the common Pb bearing wolframite, also the ^{207}Pb correction may be preferable to get the $^{206}Pb/^{238}U$ age. (3) The closure temperature of wolframite U-Pb system: The closure temperature of wolframite with respect to the U-Pb system has not been evaluated yet. (4) Matrix effect: Wolframite is in between the isomorphous solid-solution ferberite ($FeWO_4$) and hübnerite ($MnWO_4$). There is no investigation to evaluate the matrix effect between different end members using laser probe or ion probe. Compared with laser probe, ion probe tends to be more sensitive to matrix effect, which needs to be further verified. (5) Wolframite is commonly formed in medium to low temperature hydrothermal deposits, susceptible to hydrothermal alteration (such as scheelite, etc.): It is necessary to identify and confirm the mineralization stages of wolframite before performing U-Pb dating. Also, the backscattering (BSE) and cathodoluminescence (CL) images are subjected to the inhibition of iron, and they may not be able to reveal the different mineralization periods and stages. Therefore, detailed petrographic work (e.g. energy spectrum and electron probe analysis, etc.) is an important step for the reliable interpretation of wolframite U-Pb age (Romer and Lüders, 2006; Pfaff et al., 2009; Lecumberri-Sanchez et al., 2014; Harlaux et al., 2018a; Legros, 2017; Legros et al., 2020; Deng et al., 2019; Tang et al., 2020).

In summary, with the growing development and establishment of an *in situ* wolframite U-Pb dating protocol, the relative technique challenges are gradually being addressed.

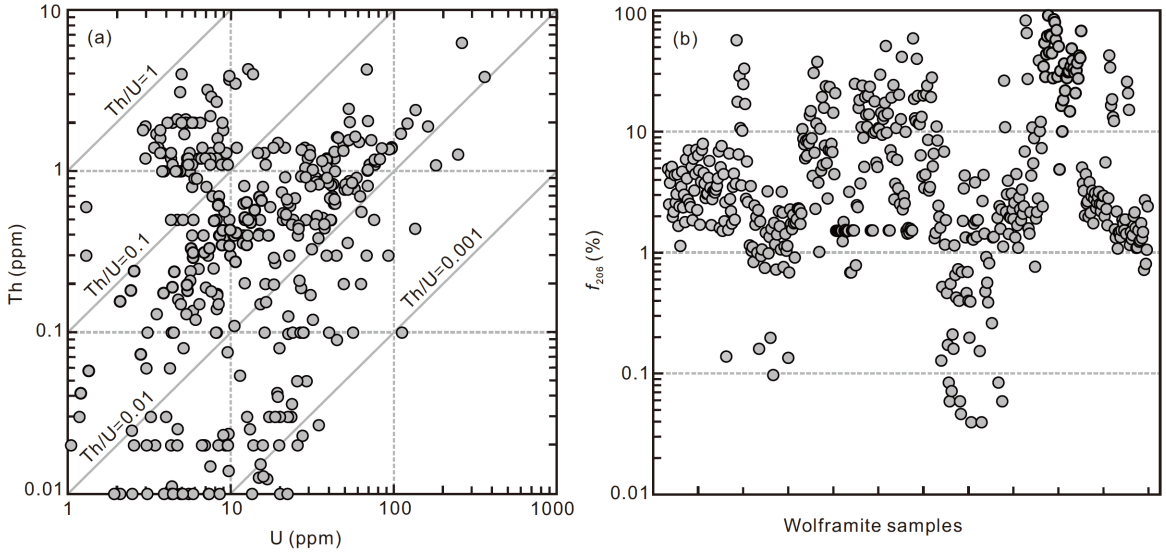

Figure 2 Th and U concentration and Th/U ratio along with variation in common Pb composition of the reported wolframite laser ablation data (data come from Harlaux et al., 2018b; Zhang et al., 2018; Deng et al., 2019; Luo et al., 2019; Legros et al., 2020; Tang et al., 2020).

It shows that the dating protocol is of far-ranging application and prospect. As strategic key metals become the hotspot in metallogenic research at home and abroad, the development of *in situ* U-Pb dating protocols for wolframite, cassiterite, columbite, tantalite, bastnäsite, monazite and other rare metal minerals will certainly make a great scientific contribution to ore deposit study in the near future.

Acknowledgements *We are indebted to the Editor-in-Chief Yongfei ZHENG for his invitation, and the anonymous reviewers for their insightful comments and advices that greatly improved this draft. We are also thankful to Dr. Yamirka Rojas-Agramonte for helping with English usage and corrections. This work was financially supported by the National Natural Science Foundation of China (Grant No. 41525012).*

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(Responsible editor: Yuanbao WU)