1.8 黑钨矿 LA-ICP-MS 微区原位 U-Pb 定年和微量元素分析

黑钨矿 U-Pb 同位素定年和微量元素含量在武汉上谱分析科技有限责任公司完成。GeolasPro HD 激光剥蚀系统由 COMPexPro 102 ArF 193 nm 准分子激光器和 MicroLas 光学系统组成，ICP-MS 型号为 Agilent 7900。本次分析的激光束斑、频率和能量密度分别为××μm、××Hz 和 5 J/cm^2，激光剥蚀过程中，采用氦气作载气，氩气为补偿气以调节灵敏度，两者在进入 ICP 之前通过一个 T 型接头混合(Günther and A. Heinrich, 1999; Luo et al., 2018a)，该激光剥蚀系统中使用了信号平滑和除汞装置，以获得平滑信号并降低汞信号(Hu et al., 2014)。在剥蚀池前加入少量（4.1mg min-1）水蒸气，以提高分析准确度和精密度(Luo et al., 2018b)。每个单点分析数据包括大约 20 s 空白信号和 50 s 样品信号。锆石 91500 (Wiedenbeck et al., 1995) 作为外标以进行 Pb/U 分馏和质量歧视校正，黑钨矿 MTM 和 SHM 作为未知样品进行分析。在本研究中，MTM 和 SHM 的×次分析中获得的 $^{206}Pb/^{238}U$ 年龄加权平均值分别为***Ma、***Ma，分别与参考年龄 333.6±1.6 Ma、25.7±0.3Ma 一致(Yang et al., 2020)。玻璃标准物质 NIST610 作外标进行微量元素含量校正(Liu et al., 2010a)。对分析数据的离线处理（包括对样品和空白信号的选择、仪器灵敏度漂移校正、元素含量及 U-Pb 同位素比值和年龄计算）采用软件 ICPMSDataCal (Liu et al., 2010b) 完成。黑钨矿样品的 U-Pb 年龄谐和图绘制和年龄加权平均计算采用 Isoplot/Ex_ver3 (Ludwig, 2003) 完成。

1.8 In-situ U-Pb dating and trace element analysis of Wolframite by LA-ICP-MS

U-Pb dating and trace element analyses of Wolframite were conducted at the Wuhan SampleSolution Analytical Technology Co., Ltd., Wuhan, China. Laser sampling was performed using a GeolasPro HD laser ablation system that consists of a COMPexPro 102 ArF excimer laser (wavelength of 193 nm and maximum energy of 200 mJ) and a MicroLas optical system. An Agilent 7900 ICP-MS instrument was used to acquire ion-signal intensities. All analyses were performed with a laser spot size of x μm, a repetition rate of x Hz and a fluence of 5 J/cm^2 in this study. The Helium was used as the carrier gas in the ablation cell and merged with argon (makeup gas) behind the ablation cell (Günther and A. Heinrich, 1999; Luo et al., 2018a). A signal-smoothing and mercury-removing device was used in this laser ablation system to obtain smooth signals and reduce the mercury signal (Hu et al., 2014). A small amount of (4.1 mg min^{-1}) water vapor was added before the ablation cell to improve the analytical accuracy and precision (Luo et al., 2018b). Each single-spot analysis consisted of 20 seconds of background signal acquisition followed by 50 seconds

of ablation. Zircon 91500 (Wiedenbeck et al., 1995) was used as an external standard to correct the Pb/U fractionation and instrumental mass discrimination; Wolframite MTM and SHM are analyzed as an unknown. The obtained weighted average $^{206}Pb/^{238}U$ ages in x analyses of MTM and SHM is ***Ma、***Ma in this study, which are consistent with the reference age of 333.6 ± 1.6 Ma、25.7 ± 0.3Ma (Yang et al., 2020). The trace element compositions of Wolframite were calibrated against NIST 610 glass as an external calibration (Liu et al., 2010a). Off-line selection and integration of background and analyte signals, time-drift correction, and quantitative calibration for trace element analyses and U-Pb dating were performed by ICPMSDataCal (Liu et al., 2010b). Concordia diagrams and weighted mean calculations were made using Isoplot/Ex_ver3 (Ludwig, 2003).

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