5.6 全岩 Pb 同位素比值分析

全岩 Pb 同位素前处理和测试由武汉上谱分析科技有限责任公司完成。

前处理流程：

前处理在配备 100 级操作台的千级超净室完成。样品消解：（1）将 200 目样品置于 105℃烘箱中烘干 12 小时；（2）准确称取粉末样品 50-200mg 置于 Teflon 溶样弹中；（3）先后依次缓慢加入 1-3ml 高纯 HNO_3 和 1-3ml 高纯 HF；（4）将 Teflon 溶样弹放入钢套，拧紧后置于 190℃烘箱中加热 24 小时以上；（5）待溶样弹冷却，开盖后置于 140℃电热板上蒸干，然后加入 1ml HNO_3 并再次蒸干；（6）用 1.0M HBr 溶解样品，待上柱分离。化学分离：用离心机将样品离心后，取上清液上柱。柱子填充 AG 树脂。用 1.0M HBr 淋洗去除基体元素。最终用 6.0M HCl 将 Pb 从柱上洗脱并收集。收集的 Pb 溶液蒸干后等待上机测试。

仪器测试流程：

Pb 同位素分析采用德国 Thermo Fisher Scientific 公司的 MC-ICP-MS（Neptune Plus）。仪器配备 9 个法拉第杯接收器。^{204}（Pb+Hg）、^{206}Pb、^{207}Pb、^{208}Pb、^{203}Tl、^{205}Tl 和 ^{202}Hg 同时被 7 个接收器接收。其中 ^{202}Hg 被用于监控并校正 ^{204}Hg 对 ^{204}Pb 同位素的同质异位素干扰，^{204}Hg/^{202}Hg 天然比值采用 0.2301。MC-ICP-MS 采用了 Jet+X 锥组合和干泵以提高仪器灵敏度。根据样品中的 Pb 含量，50 μl/min-100 μl/min 两种微量雾化器被选择使用。Alfa 公司的 Pb 单元素溶液被用于优化仪器操作参数。Pb 国际标准溶液 NIST 981 （200μg/L）作为质量监控和外部校正标样，^{208}Pb 的信号一般高于 6 V。每个标样和样品中加入一定量的 Tl 溶液（NBS SRM 997），^{205}Tl 信号控制在 4-5 之间。Tl 拖尾对 ^{204}Pb 的干扰没有被观察到。数据采集由 8 个 blocks 组成，每个 block 含 10 个 cycles，每个 cycle 为 4.194 秒。Pb 同位素的仪器质量分馏采用假内标指数法则校正（Russell et al. 1978）：

$$R_m^{\frac{i}{j}} = R_T^{\frac{i}{j}}\left(\frac{m_i}{m_j}\right)^f$$

公式中 i 和 j 指示同位素质量数，R_m 和 R_T 分别代表样品的测试比值和参考比值（推荐值），f 指仪器质量分馏因子。^{205}Tl/^{203}Tl 被用于计算 Pb 的质量分馏因子（2.38714，NIST SRM 997 证书值）。由于 Tl 的分馏行为与 Pb 分馏行为存在一定差别，因此 NIST 981 被用作外标对数据进行二次校正。实验流程采用两个 Pb 同位素标样（NIST 981 和 AlfaPb）之间插入 7 个样品进行分析。全部分析数据采用专业同位素数据处理软件“Iso-Compass”进行数据处理（Zhang et al., 2020）。NIST 981 的 ^{20x}Pb/^{204}Pb 的外部测试精度达到 0.03%（2RSD）。NIST 981 的推荐值采用 ^{208}Pb/^{204}Pb=36.7262±31，^{207}Pb/^{204}Pb=15.5000±13，^{206}Pb/^{204}Pb=16.9416±13（n=119，Baker et al. 2004）。

BCR-2（玄武岩）（参考标准物质及推荐值以报告为准）被选择作为流程监控标样。BCR-2 的 $^{20x}Pb/^{204}Pb$ 分析测试值为 $^{208}Pb/^{204}Pb$=38.736±17，$^{207}Pb/^{204}Pb$=15.628±3，$^{206}Pb/^{204}Pb$=18.756±10（2SD, n=22），与推荐值 $^{208}Pb/^{204}Pb$=38.725±22，$^{207}Pb/^{204}Pb$=15.621±4，$^{206}Pb/^{204}Pb$=18.753±8（Zhang and Hu 2020）在 0.03%误差范围内一致。数据表明，本实验流程可以对样品进行有效分离，分析准确度和精密度满足高精度的 Pb 同位素分析。

本测试方法适用 Pb 含量>2ppm 的岩石样品，保证样品 $^{20x}Pb/^{204}Pb$ 测试内精度（2RSE）0.002%~0.025%），测试准确度优于 0.03%。Pb 含量低于 2ppm 的岩石样品，测试精度和准确度会受到影响，影响程度受样品 Pb 含量控制。低 Pb 样品分析请事先咨询技术人员，确保样品分析质量。

5.6 Scheme for Pb isotope ratio analyses using MC-ICP-MS

All chemical preparations were performed on class 100 work benches within a class 1000 overpressured clean laboratory. **Sample digestion:** (1) Sample powder (200 mesh) was placed in an oven at 105 °C for drying of 12 hours; (2) 50–200 mg sample powder was accurately weighed and placed in a Teflon bomb; (3) 1-3 ml HNO_3 and 1-3 ml HF were added into the Teflon bomb; (4) Teflon bomb was putted in a stainless steel pressure jacket and heated to 190 °C in an oven for >24 hours; (5) After cooling, the Teflon bomb was opened and placed on a hotplate at 140 °C and evaporated to incipient dryness, and then 1 ml HNO_3 was added and evaporated to dryness again; (6) The sample was dissolved in 1.0 mL of 1.0 M HBr. **Column chemistry:** After centrifugation, the supernatant solution was loaded into an ion-exchange column packed with AG resin. After complete draining of the sample solution, columns were rinsed with 1.0 M HBr to remove undesirable matrix elements. Finally, the Pb fraction was eluted using 6.0 M HCl and gently evaporated to dryness prior to mass spectrometric measurement.

Pb isotope analyses were performed on a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Dreieich, Germany) at the Wuhan Sample Solution Analytical Technology Co., Ltd, Hubei, China. The Neptune Plus, a double focusing MC-ICP-MS, was equipped with seven fixed electron multiplier ICs and nine Faraday cups fitted with 10^{11} Ω resistors. The faraday collector configuration of the mass system was composed of an array to monitor ^{204}(Pb+Hg）、^{206}Pb、^{207}Pb、^{208}Pb、^{203}Tl、^{205}Tl and ^{202}Hg. The large dry interface pump (120 m^3 hr^{-1} pumping speed) and newly designed X skimmer cone and Jet sample cone were used to increase the instrumental sensitivity. A Pb single element solution from Alfa (Alfa Aesar, Karlsruhe, Germany) was used to optimize instrument operating parameters. An aliquot of the international standard solution of 200 μg L^{-1} NIST 981 was

regularly used for evaluating the reproducibility and accuracy of the instrument. Typically, the signal intensities of $^{208}Pb^{+}$ in NIST 981 were > ~6.0 V. The Pb isotopic data were acquired in the static mode at low resolution. The routine data acquisition consisted of ten blocks of 10 cycles (4.194 s of integration time per cycle). The total time of one measurement lasted about 7 minutes.

The exponential law, which was initially developed for TIMS measurement (Russell et al. 1978) and remains the most widely accepted and utilized with MC-ICP-MS, was used to assess the instrumental mass discrimination in this study. Mass discrimination correction was carried out via normalization to a $^{205}Tl/^{203}Tl$ ratio of 2.38714 (the certified value of NIST SRM 997). All data reduction for the MC-ICP-MS analysis of Pb isotope ratios was conducted using "Iso-Compass" software (Zhang et al. 2020). Because of the difference in mass bias behaviors between Pb and Tl, all measured $^{20x}Pb/^{204}Pb$ ratios of unknown samples were normalized to the well-accepted NIST 981 values of $^{208}Pb/^{204}Pb$=36.7262±31，$^{207}Pb/^{204}Pb$=15.5000±13，$^{206}Pb/^{204}Pb$=16.9416±13 (n=119，Baker et al. 2004). One NIST 981 standard was measured every seven samples analyzed. Analyses of NIST 981 standard yielded external precisions of 0.03% (2RSD) for $^{20x}Pb/^{204}Pb$ ratios. In addition, the USGS reference materials BCR-2 (basalt), (maybe different, the test report shall prevail) yielded results of $^{208}Pb/^{204}Pb$=38.736±17, $^{207}Pb/^{204}Pb$=15.628±3, $^{206}Pb/^{204}Pb$=18.756±10 (2SD, n=22)，respectively, which are identical within an error of 0.03% to their published values (Zhang and Hu 2020).

References

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