5.12 全岩 Mg 同位素比值分析

全岩 Mg 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：根据样品中的 MgO 含量，称取包含 20 μg Mg 的样品粉末置于溶样弹中，加入高浓度 HNO3 -HF 混合酸（1:1，v/v），套上钢套放入烘箱，190℃消解 48 小时。待样品完全冷却后取下钢套，将样品蒸干后加入 1ml 高浓度 HNO3，再蒸干，此步骤重复 2 次，完全去除四氟化硅。接着，加入 1ml 高浓度 HNO3 和 2ml 高纯水，套上钢套放入烘箱，190℃消解 12 小时，直至样品溶液澄清透明完全消解。将消解后的溶液蒸干用高浓度 HNO3 进行转介质，最终将蒸干后的溶液定容在 1.5N HNO3 中用于化学分离。

纯化分离：整个分离过程参考 Wang et al. (2022)共需进行三步进行分离。

第一步：将消解好的样品加入装有 AG50W-X8 阳离子树脂（200~400 目）的柱子中并接样，再用 20ml 的 1.5N HNO3 淋洗样品并继续接样。最后用 6N HCl 洗脱树脂中剩余的基体元素残留（如 Al，Fe，Ca）；

第二步：将步骤一中接取的 Mg 溶液蒸干后加入到之前的柱子中，然后用 1N HNO3 淋洗杂质元素，再用 17ml 1N HNO3 完全洗脱 Mg；

第三步：重复步骤二，再次淋洗 Mg 溶液中的杂质元素。

经过三步化学纯化之后，大部分基体元素与 Mg 分离的较为彻底。同时 Mg 的回收率为 100%±3%，全流程空白小于 12ng。

仪器测试流程：

Mg 同位素在武汉上谱分析公司使用 Neptune plus 型多接收电感耦合等离子质谱仪进行分析。测试时采用湿法进样和低分辨模式，样品进样浓度为 200ppb，介质为 2% HNO3。通过样品-标样间插法(SSB)对仪器分馏进行校正，所有 Mg 同位素数据相对于标样 GSB Mg 测试，然后根据 GSB Mg 相对于 Mg 基准溶液 DSM3 转换得到(Bao et al., 2019)。计算公式如下：

$\delta^{i}Mg\ (‰) = [(^{i}Mg/^{24}Mg)_{sample} / (^{i}Mg/^{24}Mg)_{GSB\ Mg} - 1]\times10^{3}$ (其中 i 可以是 25 或者 26)

$\delta^{26/24}Mg_{DSM3} = \delta^{26/24}Mg_{smp\text{-}GSB\ Mg} - 2.05$

$\delta^{25/24}Mg_{DSM3} = \delta^{25/24}Mg_{smp\text{-}GSB\ Mg} - 1.06$

每一批测试的样品都包括有至少两个国际地质标样来监测仪器的测试状态及样品前处理

流程，以确保样品数据的准确性与精确性，上谱分析长期测试结果表明其同位素组成在误差范围内和前人报道数据一致（BCR-2，AGV-2，BHVO-2，GSP-2，推荐值及参考文献以报告为准），本实验室长期的 $\delta^{26}Mg$ 测试精度为 0.06‰。

5.12 Mg isotope analysis using MC-ICP-MS

All chemical preparations were performed on class 100 work benches within a class 1000 overpressured clean laboratory. **Sample digestion：** Based on the MgO content of the sample, a portion of each sample powder containing 20 μg of Mg was weighed into Teflon bombs. Then, 2ml HNO_3-HF mixed acid (1:1, v/v) was added, and the sealed bomb was placed in an electric oven at 190℃ for 48 hours to digest the sample. After cooling, the bomb was opened and placed on a hotplate to evaporated to dryness. This was followed by adding 1 ml HNO_3 and evaporating to dryness. This step was repeated twice to completely remove fluoride. After that, the residue was re-dissolved by adding 1 ml of HNO_3 and 2 ml of ultra-pure water. The bomb was resealed and placed in an electric oven at 190℃ for 12 hours to obtain a clear digestion solution. The final solution was evaporated and re-dissolved in 200 μl 1.5N HNO_3 for chemical separation.

Magnesium separation: The chemical separation procedure for geological samples followed method outlined by Wang et al. (2022), and involved three sequential column separation steps. Step one: The digested sample was loaded into a column filled with AG50W-X8 resin (200~400 mesh), and subsequently rinsed with 20 ml of 1.5N HNO_3. All fractions from both loading and rinsing were collected for the quantitative recovery of Mg. The residual matrix elements (such as Al, Fe, Ca) are then eluted from the resin using 6N HCl. Step two: The Mg solution obtained in step one was evaporated and loaded to the same column which was pre-cleared. Matrix elements are washed with 1N HNO_3, and the Mg fraction was collected through the elution with 17 ml 1N HNO_3. Step three: Repeat step two to further improve the purity of the Mg solution.

After the three-column chemical purification process, all the interference elements were effectively separated from Mg. The recovery of Mg obtained was 100%±3%, and the total blank of the entire process was less than 12 ng.

Mass spectrometry measurements: Mg isotopic measurement was performed on a Thermo Fisher Scientific Neptune Plus MC-ICP-MS at Wuhan Sample Solution Analytical Technology Co., Ltd. Measurements were performed in low resolution and sample solution were introduced into the plasma at 200pb Mg in 2% HNO3 (m/m). The sample-standard bracketing (SSB) method was used to correct the instrumental mass bias during Mg isotopic analysis. All Mg isotope data are measured

relative to the GSB Mg standard, and then converted to DSM3 based results according to the relative value between GSB Mg and DSM3 proposed by Bao et al., 2019. The converted formula is as follows:

$$d^{i}Mg\ (‰) = [(^{i}Mg/^{24}Mg)_{sample} / (^{i}Mg/^{24}Mg)_{GSB\ Mg} - 1]\times 10^{3} \quad (\text{where } i = 25 \text{ or } 26)$$

$$\delta^{26/24}Mg_{DSM3} = \delta^{26/24}Mg_{smp\text{-}GSB\ Mg} - 2.05$$

$$\delta^{25/24}Mg_{DSM3} = \delta^{25/24}Mg_{smp\text{-}GSB\ Mg} - 1.06$$

Each batch of samples includes at least two international geological reference standards to monitor the performance of instrumental measurement and chemical separation, ensuring the accuracy and precision of the results. Repeated measurements of the geological standards (e.g., BCR-2, AGV-2, BHVO-2 and GSP-2, the test report shall prevail) in our laboratory were consistent with previously reported data, and the long-term reproducibility of $\delta^{26}Mg$ was better than 0.06‰.

References

Bao, Z.-A., K.-J. Huang, T.-Z. Huang, B. Shen, C.-L. Zong, K.-Y. Chen, and H.-L. Yuan, 2019, Precise magnesium isotope analyses of high-K and low-Mg rocks by MC-ICP-MS: Journal of Analytical Atomic Spectrometry, v. 34, p. 940-953.

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