

Table S4 - Cu-isotope rock standard data, BHVO-2

USGS Std	Published value	PSU August 2018	PSU December 2019	PSU Oct 2020	Rutgers Dec 2020	PSU Jan 2021	Rutgers Feb 2021	$\delta^{65}\text{Cu}$ (per mil)	2σ	n
BHVO-2	0.14	0.19	0.12	0.13	0.14	0.16	0.14	0.15	0.05	6

Two different values for BHVO-2 have been reported in the literature. A value of 0 per mil was determined by Sossi et al. (2015) and several other papers using Zn and Ni to correct for mass bias. In contrast, Liu et al. (2015) and several other papers reported a $\delta^{65}\text{Cu}$ value for BHVO-2 of $+0.14\text{‰} \pm 0.05$ using sample-standard bracketing to correct for mass bias. Neither of these values overlap within the reported analytical errors. Since these publications went into print, the following papers have reported values overlapping with Lui et al. (2015): Huang et al. (2016), Lv et al. (2016), Moynier et al. (2017), Liu et al. (2019), Xia et al. (2019), and Liu et al. (2021). We obtained a value for BHVO-2 of $+0.15 \pm 0.05 \text{‰}$ ($2s$, $n=6$) over a 5-year period using the sample-standard bracketing approach, i.e., our data are consistent with the reported value for BHVO-2 of Liu et al. (2015).

References:

- Huang, J., Liu, S.-A., Gao, Y., Xiao, Y., & Chen, S. (2016). Copper and zinc isotope systematics of altered oceanic crust at IODP Site 1256 in the eastern equatorial Pacific, *Journal of Geophysical Research. Solid Earth*, 121, 7086–7100, doi:10.1002/2016JB013095
- Liu, S.-A., Huang, J., Liu, J., Wörner, G., Yang, W., Tang, Y.-J., Chen, Y., Tang, L., Zheng, J., & Li, S. (2015). Copper isotopic composition of the silicate Earth. *Earth and Planetary Science Letters*, 427, 95-103. <https://doi.org/10.1016/j.epsl.2015.06.061>
- Liu, S.-A., Liu, P.-P., Lv, Y., Wang, Z.-Z., Dai, J.-G., (2019). Cu and Zn isotope fractionation during oceanic alteration: Implications for Oceanic Cu and Zn cycles. *Geochimica et Cosmochimica Acta*, 257, 191–205.
- Liu, J.H., Zhou, L., Wang, Q., Feng, L.P., Shen, J., Herrmann, A.D., Algeo, T.J. (2021) Copper isotope evidence of particulate shuttle dynamics in the Late Pennsylvanian North American Midcontinent Sea, with implications for glacio-eustatic magnitude. *Geochimica et Cosmochimica Acta*, 297, 1–23.
- Lv, Y., Liu, S.-A., Zhu, J.-M., & Li, S. (2016). Copper and zinc isotope fractionation during deposition and weathering of highly metalliferous black shales in central China. *Chemical Geology*, 445, 24–35.
- Moynier, F., Vance, D., Fujii, T., & Savage, P. (2017). The Isotope Geochemistry of Zinc and Copper. *Reviews in Mineralogy and Geochemistry*, 82, DOI: 10.2138/rmg.2017.82.13
- Sossi, P. A., Halverson, G. P., Nebel, O., & Eggins, S. M. (2015). Combined Separation of Cu, Fe and Zn from Rock Matrices and Improved Analytical Protocols for Stable Isotope Determination: *Geostandards and Geoanalytical Research*, 39 (2), 129-149. <https://doi.org/10.1111/j.1751-908X.2014.00298.x>
- Xia, Y., Kiseeva, E.S., Wade, J., Huang, F. (2019) The effect of core segregation on the Cu and Zn isotope composition of the silicate Moon. *Geochemical Perspectives Letters*, doi: 10.7185/geochemlet.1928