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A data reduction scheme to use inhomogeneous materials as primary standards for non-U-Pb geochronology via LA-ICP-MS

DANIIL POPOV

no affiliation

Presenting Author: d.vs.popov@gmail.com

Recent developments in LA-ICP-MS, particularly the advent of reaction cells, solved the problem of isobaric interferences in many isotope systems, such as K-Ca, Rb-Sr and Lu-Hf, and thereby provided a variety of new avenues for in situ geochronology. However, there is another challenge to overcome before these isotope systems can be exploited at full capacity, which is the lack of matrix-matched primary standards to correct for elemental fractionation (hereafter, *k*-standards).

Ideally, *k*-standards should be chemically and isotopically homogeneous materials that are isostructural to the analysed samples. Since finding such materials is not easy, many recent studies relied on using pressed nanoparticulate powder tablets in their place. However, this approach can reportedly introduce systematic errors of up to 7 % into the obtained dates, which result from the difference in the ablation properties between polycrystalline aggregates that serve as *k*-standards and individual uninterrupted crystals that are being dated [1]. An alternative route would be using a crystal with heterogeneously distributed parent and daughter isotopes in place of a *k*-standard, which should be possible if the variations of its composition follow an isochron. While common in U-Pb geochronological applications of LA-ICP-MS, with the exception of only a few studies, this route has not been employed for other isotope systems.

One possible reason why inhomogeneous materials were not used as k-standards in non-U-Pb geochronology via LA-ICP-MS is that there was no data reduction scheme for doing so. Last year, I have published such a reduction scheme [2]. In addition to using an inhomogeneous *k*-standard, this scheme invokes an additional reference material to correct for mass-dependent fractionation (hereafter *l*-standard). Due to unfortunate life circumstances, I have not been able to test this reduction scheme with the real world data. However, it works as intended when applied to synthetic data, an example of which is provided in the attached table, where each of the values in the Results sections is reproduced by Monte Carlo simulations to within 1 %.

[1] Redaa et al. (2021), *JAAS* 36(2), 322-344. https://doi.org/10.1039/D0JA00299B

[2] Popov (2022), *Geochronology* 4, 399–407. https://doi.org/10.5194/gchron-4-399-2022

Common variables

decay constant: $\lambda = 1.393{\cdot}10^{-5}$, $\sigma_\lambda = 0.3\,\%$
l-standard: $Y^+ = 50$, $\sigma_{Y^+} = 0.5\,\%$
k-standard: $t = 1000$, $\sigma_t = 1.8\,\%$; $Y_0 = 10$, $\sigma_{Y_0} = 0.2\,\%$; $X^* = 100$
unknown: $Y_{0u} = 0.5$, $\sigma_{Y_{0u}} = 1\,\%$

Batch 1 (l-standard 'analyses' yield $y^+ = 5$, $\sigma_{y^+} = 0.5\,\%$, so $l = 10$)

k-standard	x	σ_x, %	y	σ_y, %	$\rho_{x,y}$
1	924.49	0.13	13.9682	0.13	0.411
2	820.59	0.41	12.5108	0.41	0.136
3	565.32	0.56	8.9300	0.56	0.529
4	937.29	0.43	14.1478	0.43	0.098
5	527.86	0.24	8.4046	0.24	0.248
6	215.20	0.12	4.0188	0.12	0.062
7	405.66	0.18	6.6904	0.18	0.051
8	133.07	0.20	2.8666	0.20	0.447
unknown	x_u	σ_{x_u}, %	y_u	σ_{y_u}, %	ρ_{x_u,y_u}
1	816.82	0.068	5.18629	0.079	0.513
2	1290.11	0.085	8.16246	0.112	0.649
3	423.96	0.114	2.71595	0.138	0.545
4	9547.23	0.209	60.08477	0.120	0.446
5	61.15	0.363	0.43452	0.060	0.061

Batch 2 (l-standard 'analyses' yield $y^+ = 500$, $\sigma_{y^+} = 0.5\,\%$, so $l = 0.1$)

k-standard	x	σ_x, %	y	σ_y, %	$\rho_{x,y}$
1	71958	0.37	1109.40	0.37	0.011
2	87384	0.13	1325.78	0.13	0.484
3	24110	0.27	438.20	0.27	0.067
4	11713	0.23	264.31	0.23	0.076
5	71051	0.24	1096.67	0.24	0.076
6	60271	0.25	945.45	0.25	0.014
7	15063	0.32	311.29	0.32	0.132
8	12172	0.35	270.74	0.35	0.269
unknown	x_u	σ_{x_u}, %	y_u	σ_{y_u}, %	ρ_{x_u,y_u}
1	8.1428	0.145	5.0512	0.146	0.907
2	7.3238	0.134	5.0461	0.220	0.067
3	7.7219	0.059	5.0486	0.070	0.576
4	4383.1609	0.083	32.5621	0.147	0.165
5	122.8432	0.219	5.7725	0.099	0.205

Results for Batch 1

k-standard 1 (Eq. 3-4): $k = 10$, $\sigma_{k\ int} = 0.15\,\%$, $\sigma_{k\ ext} = 1.9\,\%$
all k-standards (Eq. 7-8): $k_{wm} = 10$, $\sigma_{k_{wm}\ int} = 0.091\,\%$, $\sigma_{k_{wm}\ ext} = 2.0\,\%$
unknown 1 (Eq. 9-15): $X_u = 8168.2$, $Y_u = 51.863$, $\sigma_{X_u int} = 0.068\,\%$, $\sigma_{Y_u int} = 0.079\,\%$, $\sigma_{X_u,Y_u int} = 0.117$, $\sigma_{X_u ext} = 2.0\,\%$, $\sigma_{Y_u ext} = 0.71\,\%$, $\sigma_{X_u,Y_u ext} = 25.5$; $T_{spot} = 450$, $\sigma_{T_{spot} int} = 0.073\,\%$, $\sigma_{T_{spot} ext} = 1.8\,\%$
all unknowns (Eq. 16, 27-28): $b = 0.0062882$, $\sigma_{b\ int} = 0.050\,\%$, $\sigma_{b\ ext} = 1.8\,\%$; $T_{isochron} = 450$, $\sigma_{T_{isochron} int} = 0.050\,\%$, $\sigma_{T_{isochron} ext} = 1.8\,\%$

Results for Batches 1+2

all unknowns (Eq. 17-28): $b_{wm} = 0.0062882$, $\sigma_{b_{wm} int} = 0.048\,\%$, $\sigma_{b_{wm} ext} = 1.8\,\%$; $T_{isochron} = 450$, $\sigma_{T_{isochron} int} = 0.048\,\%$, $\sigma_{T_{isochron} ext} = 1.8\,\%$

Y^+ and y^+ are the true and measured daughter-to-common isotope ratios for the l-standard. All other variables are explained in my paper.