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# Short communication: On the potential use of materials with heterogeneously distributed parent and daughter isotopes as primary standards for non-U-Pb geochronological applications of laser ablation inductively coupled mass spectrometry (LA-ICP-MS)

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**Abstract.** Many new geochronological applications of laser ablation inductively coupled mass spectrometry (LA-ICP-MS) have been proposed in recent years. One of the problems associated with this rapid growth is the lack of chemically and
10  isotopically homogeneous matrix-matched primary standards to control elemental fractionation during LA-ICP-MS analysis. In U-Pb geochronological applications of LA-ICP-MS this problem is often addressed by utilising matrix-matched primary standards with variable chemical and isotopic compositions. Here I derive a set of equations to adopt this approach for non-U-Pb geochronological applications of LA-ICP-MS.

## 1 Introduction

15  The use of laser ablation inductively coupled mass spectrometry (LA-ICP-MS) for in situ geochronology is growing rapidly, and recent years have seen this technique being applied to many new minerals and isotope systems. Examples include in situ U-Pb dating of apatite (Chew et al., 2014, 2011), carbonates (Roberts et al., 2017; Li et al., 2014; Guillong et al., 2020) and epidote (Peverelli et al., 2021), Rb-Sr dating of micas (Hogmalm et al., 2017; Zack and Hogmalm, 2016) and celadonite (Laureijs et al., 2021), Lu-Hf dating of garnet, apatite and xenotime (Simpson et al., 2021), and a new approach to Re-Os
20  dating of molybdenite (Hogmalm et al., 2019). One important challenge associated with this rapid growth is the development of matrix-matched primary standards to correct for elemental fractionation during LA-ICP-MS analysis. Ideally, primary standards should be chemically and isotopically homogeneous and isostructural to the analysed minerals. However, finding or synthesising such materials is not trivial. Therefore, recent studies relied on some alternative solutions, including the use (i) matrix-matched standards with variable chemical and isotopic composition (e.g. Chew et al., 2014) and (ii)
25  nanoparticulate pressed powder tablets as substitutes for chemically and isotopically homogeneous matrix-matched standards (e.g. Hogmalm et al., 2017).

Matrix-matched primary standards with variable contents of parent and daughter isotopes are often used in U-Pb geochronological applications of LA-ICP-MS. Chew et al. (2014) proposed an approach for dating common Pb-bearing

phases, in which primary standards with variable contents of common Pb are used to characterise U-Pb fractionation. This is

30    achieved (among other options) by applying the [207]Pb-based correction for common Pb to individual primary standard analyses before factors to correct for U-Pb fractionation are calculated from them, such that the latter step only relies on comparing the observed and expected $^{238}$U/$^{206}$Pb$_{radiogenic}$ ratios (as opposed to using the $^{238}$U/$^{206}$Pb$_{total}$ ratios). In other words, factors for U-Pb fractionation correction are calculated by comparing the observed and expected intercepts with the concordia in the Tera-Wasserburg space for individual primary standard analyses (Fig. 1a). A similar approach was adopted

35    by Li et al. (2014), Roberts et al. (2017) and Guillong et al. (2020), who first used chemically and isotopically homogeneous non-matrix-matched primary standards to correct for any drift in U-Pb fractionation during analytical sessions, and then used matrix-matched primary standards with variable contents of common Pb to calculate correction factors for matrix-dependent U-Pb fractionation. The latter was done by plotting multiple primary standard analyses in the Tera-Wasserburg diagram to obtain discordias and compare their observed and expected intercepts with the concordia.

40    Apparently, there is only one non-U-Pb geochronological application of LA-ICP-MS where a material with variable contents of parent and daughter isotopes was essentially used as a primary standard, which is the pioneering work on in situ Rb-Sr dating by Zack and Hogmalm (2016). These authors calculated what factor is needed to correct for Rb-Sr fractionation in one biotite sample with known age to obtain an isochron of that age and then applied it to other samples measured on the same day. The idea was not developed further, and subsequent studies relied on using nanoparticulate pressed powder tablets

45    as substitutes for chemically and isotopically homogeneous matrix-matched primary standards (Hogmalm et al., 2017, 2019; Olierook et al., 2020; Li et al., 2020; Tillberg et al., 2021). However, the ablation properties of nanoparticulate pressed powder tablets are different from those of single crystals, and while they perform better as primary standards compared to glasses, Rb-Sr dates obtained by using them can be offset from the expected values by several % (mostly up to 4 %, occasionally up to 7 % in tests of Redaa et al., 2021). Therefore, the quest for matrix-matched standards remains open. With

50    this communication I aim to highlight that the idea of using materials with heterogeneously distributed parent and daughter isotopes as primary standards may have been abandoned prematurely and provide a set of equations for doing so.

## 2 Proposed Solution

Presumably, one of the reasons why the idea of using primary standards with variable contents of parent and daughter isotopes was abandoned in non-U-Pb geochronological applications of LA-ICP-MS is the absence of a clear approach to

55    calculate factors for elemental fractionation correction and their uncertainties. Clearly, these factors can be estimated by plotting two-point normal or inverse isochrons based on individual primary standard analyses and finding by what coefficients the measured elemental ratios need to be multiplied to bring the slopes of the apparent normal or inverse isochrons to the true values (Fig. 1b, c). These factors can also be estimated by calculating and comparing the observed and expected intercepts with the horizontal axis in the inverse isochron diagram, which is analogous to the use of the Tera-

60    Wasserburg diagram in U-Pb geochronological applications of LA-ICP-MS (Fig. 1c). But how to calculate elemental

fractionation correction factors in an efficient way? And how to estimate their uncertainty, so that individual primary standard analyses can be adequately compared? Below I derive equations that can be used to do so.

In the normal isochron space, the true composition of a primary standard with heterogeneously distributed parent and daughter isotopes is given by Eq. (1):

65 
$$Y = Y_0 + X(e^{\lambda t} - 1) \,, \tag{1}$$

where $Y$ is the daughter to common isotope ratio (e.g., $^{87}Sr/^{86}Sr$), $Y_0$ is the initial daughter to common isotope ratio (e.g., $^{87}Sr/^{86}Sr_0$), $X$ is the parent to common isotope ratio (e.g., $^{87}Rb/^{86}Sr$), $\lambda$ is the decay constant and $t$ is the age of the primary standard. The analysis of this primary standard by LA-ICP-MS yields some proxies for the true $Y$ and $X$ values, which are the measured $y$ and $x$ values, respectively. It is generally presumed that any difference between $Y$ and $y$ is a result of mass

70 dependent fraction that can be corrected for independently of measuring the primary standard in question (e.g. Chew et al., 2011; Li et al., 2014; Hogmalm et al., 2017; Redaa et al., 2021). Provided that this is done, $Y$ can be assumed to be equal to $y$. In contrast, $X$ and $x$ are expected to be different from each other due to elemental fractionation that is heavily dependent on the matrix properties and ablation conditions (e.g. Chew et al., 2011; Li et al., 2014; Hogmalm et al., 2017; Redaa et al., 2021). Therefore, it can only be assumed that $X$ is equal to the product of $x$ and the factor $k$ needed to correct for elemental

75 fractionation. With these assumptions Eq. (1) can be modified to make Eq. (2):

$$y = Y_0 + kx(e^{\lambda t} - 1) \,, \tag{2}$$

from which it is possible to obtain an expression for $k$ given by Eq. (3):

$$k = \frac{y - Y_0}{x(e^{\lambda t} - 1)} \,. \tag{3}$$

The uncertainty of thereby calculated $k$ can be estimated using Eq. (4)

80 
$$\sigma_k^2 = \sigma_x^2 \left(\frac{-k}{x}\right)^2 + \sigma_y^2 \left(\frac{k}{(y-Y_0)}\right)^2 + 2\sigma_{x,y} \left(\frac{-k^2}{x(y-Y_0)}\right) + \sigma_{Y_0}^2 \left(\frac{-k}{(y-Y_0)}\right)^2 + 2\sigma_{Y_0,t} \left(\frac{\lambda x k^3 e^{\lambda t}}{(y-Y_0)^2}\right) +$$
$$+ \sigma_t^2 \left(\frac{-\lambda k}{1-e^{-\lambda t}}\right)^2 + \sigma_\lambda^2 \left(\frac{-tk}{1-e^{-\lambda t}}\right)^2 + 2\sigma_{\lambda,t} \left(\frac{t\lambda k^2}{(1-e^{-\lambda t})^2}\right) \,, \tag{4}$$

where only the first three terms should be used to calculate the internal uncertainty, and the entire equation should be used to calculate the external uncertainty. In principle, $\sigma_{Y_0,t}$ and $\sigma_{\lambda,t}$ should be different from zero if $t$ was determined using the same $Y_0$ and $\lambda$ as in the equations above (i.e. the age of the primary standard is not determined using some other method).

85 Provided that this is the case, $\sigma_{Y_0,t}$ and $\sigma_{\lambda,t}$ can be estimated using Eq. (5-6):

$$\sigma_{\lambda,t} = -\frac{t\sigma_\lambda^2}{\lambda} \,, \tag{5}$$

$$\sigma_{Y_0,t} = -\frac{\sigma_{Y_0}^2}{\lambda X^* e^{\lambda t}} \,, \tag{6}$$

where $X^*$ is the parent to common isotope ratio used to determine $t$. If $t$ was determined by fitting an isochron rather than using a single analysis, then $X^*$ could probably be approximated by the weighted mean for the analyses used in isochron fitting. Note that for well-characterised primary standards $\sigma_{Y_0,t}$ will most likely be negligibly small.

Following the same logic and assumptions to derive expressions for the inverse isochron space yields Eq. (7-12):

$$Y' = Y'_0 + X'Y'_0(1 - e^{\lambda t}) , \tag{7}$$

$$y' = Y'_0 + kx'Y'_0(1 - e^{\lambda t}) , \tag{8}$$

$$k = \frac{y' - Y'_0}{x'Y'_0(1 - e^{\lambda t})} , \tag{9}$$

$$\sigma_k^2 = \sigma_{x'}^2 \left(\frac{-k}{x'}\right)^2 + \sigma_{y'}^2 \left(\frac{k}{y' - Y'_0}\right)^2 + 2\sigma_{x',y'} \left(\frac{-k^2}{x'(y' - Y'_0)}\right) + \sigma_{Y'_0}^2 \left(\frac{-y'k}{Y'_0(y' - Y'_0)}\right)^2 + 2\sigma_{Y'_0,t} \left(\frac{-\lambda x'y'k^3 e^{\lambda t}}{(y' - Y'_0)^2}\right) +$$

$$+ \sigma_\lambda^2 \left(\frac{-tk}{1 - e^{-\lambda t}}\right)^2 + \sigma_t^2 \left(\frac{-\lambda k}{1 - e^{-\lambda t}}\right)^2 + 2\sigma_{\lambda,t} \left(\frac{\lambda t k^2 e^{2\lambda t}}{(1 - e^{-\lambda t})^2}\right) , \tag{10}$$

$$\sigma_{\lambda,t} = -\frac{t\sigma_\lambda^2}{\lambda} , \tag{11}$$

$$\sigma_{Y'_0,t} = -\sigma_{Y_0,t} = \sigma_{Y'_0}^2 \frac{1 + X'^*(1 - e^{\lambda t})}{\lambda X'^* Y'_0 e^{\lambda t}} , \tag{12}$$

where $Y'$ and $y'$ are the true and measured common to daughter isotope ratios (e.g., $^{86}Sr/^{87}Sr$), $Y'_0$ is the initial common to daughter isotope ratio (e.g., $^{86}Sr/^{87}Sr_0$), $X'$ and $x'$ are the true and measured parent to daughter ratios (e.g., $^{87}Rb/^{87}Sr$), and $X'^*$ is the parent to daughter isotope ratio used to determine $t$.

Repeated primary standard analyses will yield $k_1$ to $k_N$, which could be averaged to obtain $k_{av}$ using Eq. (13):

$$k_{av} = \frac{k_1 + \cdots + k_N}{N} . \tag{13}$$

The uncertainty of $k_{av}$ is given by Eq. (14):

$$\sigma_{k_{av}}^2 = \left(\frac{\sigma_{k_1 int}^2}{N^2} + \cdots + \frac{\sigma_{k_N int}^2}{N^2}\right) + \frac{k_{av}^2(\sigma_\lambda^2 t^2 + \sigma_t^2 \lambda^2 + 2\sigma_{\lambda,t} t\lambda)}{(1 - e^{-\lambda t})^2} + a , \tag{14}$$

where the sum in parentheses provides the internal uncertainty, while the entire equation provides the external uncertainty. The term $a$ accounts for the uncertainty associated with the uncertainty in the initial daughter to common or common to daughter isotope ratio. For well-characterised primary standards, particularly for those with high parent to daughter isotope ratios, $a$ will most likely be negligibly small. I could not find an exact equation to calculate $a$ because it depends in a complex way on both the LA-ICP-MS analyses of the primary standard and the data used to determine $t$. If this becomes necessary, $a$ could probably be estimated as a simple average of the terms associated with the uncertainty in the initial daughter to common or common to daughter isotope ratio in Eq. (4, 10), which is given by Eq. (15, 16):

$$a \approx \frac{\sigma_{Y_0}^2}{N(e^{\lambda t}-1)^2}\left(\frac{1}{x_1^2}+\cdots+\frac{1}{x_N^2}\right)+\frac{2\sigma_{Y_0,t}k_{av}e^{\lambda t}}{N(e^{\lambda t}-1)^2}\left(\frac{1}{x_1}+\cdots+\frac{1}{x_N}\right),\tag{15}$$

$$a \approx \frac{\sigma_{Y_0'}^2 * k_{av}^2}{N{Y_0'}^2}\left(\frac{{y_1'}^2}{(y_1'-Y_0')^2}+\cdots+\frac{{y_N'}^2}{(y_N'-Y_0')^2}\right)+\frac{2\sigma_{Y_0,t}'\lambda k_{av}^2 e^{\lambda t}}{Y_0'(e^{\lambda t}-1)}\left(\frac{y_1'}{y_1'-Y_0'}+\cdots+\frac{y_N'}{y_N'-Y_0'}\right),\tag{16}$$

115    Following the same assumptions and notation as above, an analysis of an unknown yields $y_u$ and $y_u'$ that do not require further correction and $x_u$ and $x_u'$ that should be corrected for elemental fractionation to obtain $x_{uc}$ and $x_{uc}'$. The latter values and their external uncertainties can be calculated using Eq. (17-20):

$$x_{uc} = k_{av}x_u,\tag{17}$$

$$\sigma_{x_{uc}}^2 = \sigma_{x_u}^2 k_{av}^2 + \sigma_{k_{av}}^2 x_u^2,\tag{18}$$

120    $$x_{uc}' = k_{av}x_u',\tag{19}$$

$$\sigma_{x_{uc}'}^2 = \sigma_{x_u}^2 k_{av}^2 + \sigma_{k_{av}}^2 {x_u'}^2.\tag{20}$$

In the normal isochron space, the date of the unknown $T_{spot}$ can be calculated using Eq. (21) provided that its initial isotopic composition $y_{0u}$ is known:

$$T_{spot} = \frac{\ln\left(\frac{y_u-y_{0u}}{k_{av}x_u}+1\right)}{\lambda}.\tag{21}$$

125    The uncertainty $T_{spot}$ is given by Eq. (22):

$$\sigma_{T_{spot}}^2 = \sigma_{x_u}^2\left(\frac{y_{0u}-y_u}{x_u\lambda(y_u-y_{0u}+k_{av}x_u)}\right)^2 + \sigma_{y_u}^2\left(\frac{1}{\lambda(y_u-y_{0u}+k_{av}x_u)}\right)^2 + 2\sigma_{x_u,y_u}\left(\frac{y_{0u}-y_u}{x_u\lambda^2(y_u-y_{0u}+k_{av}x_u)^2}\right) +$$
$$+\sigma_{y_{0u}}^2\left(\frac{-1}{\lambda(y_u-y_{0u}+k_{av}x_u)}\right)^2 + \sigma_{k_{av}}^2\left(\frac{y_{0u}-y_u}{\lambda k_{av}(y_u-y_{0u}+k_{av}x_u)}\right)^2 + \sigma_\lambda^2\left(\frac{-T_{spot}}{\lambda}\right)^2,\tag{22}$$

where the first three terms provide the internal uncertainty, while the entire equation provides the external uncertainty. Note that $\sigma_{k_{av},\lambda}$ is zero, and thus the associated covariance term is absent in this and following equations.

130    If the initial isotopic composition is not known, the multi-spot isochron date $T_{isochron}$ can be calculated using Eq. (23):

$$T_{isochron} = \frac{\ln\left(\frac{b}{k_{av}}+1\right)}{\lambda}.\tag{24}$$

The uncertainty of $T_{isochron}$ is given by Eq. (25):

$$\sigma_{T_{isochron}}^2 = \sigma_b^2\left(\frac{1}{\lambda(b+k_{av})}\right)^2 + \sigma_{k_{av}}^2\left(\frac{-b}{\lambda k_{av}(b+k_{av})}\right)^2 + \sigma_\lambda^2\left(\frac{-T_{isochron}}{\lambda}\right)^2,\tag{25}$$

where the first term provides the internal uncertainty, while the entire equation provides the external uncertainty.

In the inverse isochron space, analogous expressions take form of Eq. (26-29):

$$T'_{spot} = \ln \frac{\left(1 - \frac{y'_u - y'_{0u}}{k_{av} x'_{uc} y'_{0u}}\right)}{\lambda}, \tag{26}$$

$$\sigma^2_{T'_{spot}} = \sigma^2_{x'_u}\left(\frac{y'_u - y'_{0u}}{x'_u \lambda (k_{av} x'_u y'_{0u} - y'_u + y'_{0u})}\right)^2 + \sigma^2_{y'_u}\left(\frac{-1}{\lambda(k_{av} x'_u y'_{0u} - y'_u + y'_{0u})}\right)^2 + 2\sigma_{x'_u, y'_u}\left(\frac{-(y'_u - y'_{0u})}{x'_u \lambda^2 (k_{av} x'_u y'_{0u} - y'_u + y'_{0u})^2}\right) +$$

$$+ \sigma^2_{y'_{0u}}\left(\frac{y'_u}{y'_{0u} \lambda (k_{av} x'_u y'_{0u} - y'_u + y'_{0u})}\right)^2 + \sigma^2_{k_{av}}\left(\frac{y'_u - y'_{0u}}{k_{av} \lambda (k_{av} x'_u y'_{0u} - y'_u + y'_{0u})}\right)^2 + \sigma^2_\lambda \left(\frac{-T_{spot}}{\lambda}\right)^2, \tag{27}$$

$$T'_{isochron} = \ln \frac{\left(1 - \frac{b'}{k_{av} y'_{0u}}\right)}{\lambda}, \tag{28}$$

$$\sigma^2_{T'_{isochron}} = \sigma^2_{b'}\left(\frac{-b'}{\lambda(k_{av} y'_{0u} - b')}\right)^2 + \sigma^2_{y'_{0u}}\left(\frac{b'}{\lambda y'_{0u}(k_{av} y'_{0u} - b')}\right)^2 + \sigma^2_{k_{av}}\left(\frac{b'}{\lambda k(k_{av} y'_{0u} - b')}\right)^2 + \sigma^2_\lambda \left(\frac{-T'_{isochron}}{\lambda}\right)^2, \tag{29}$$

where $T'_{spot}$ and $T'_{isochron}$ are the single- and multi-spot dates, $y'_{0u}$ is the initial isotopic composition and $b'$ is the slope of the line fitted trough the data in the inverse isochron space.

## 3 Conclusion

The above equations can be used to first calculate elemental fractionation correction factors and their uncertainties from individual analyses of primary standards with variable contents of parent and daughter isotopes, and then calculate isochron dates for individual or multiple analyses of unknowns and their uncertainties. Although it is yet to be tested how well the outlined approach performs in practice, it has two potential benefits over using non-matrix-matched primary standards and nanoparticulate pressed powder tablets as substitutes for matrix-matched primary standards. Firstly, it could be more suitable to characterise elemental fractionation in unknowns by providing better matrix matching. Secondly, it could reduce time needed to analyse one batch of unknowns due to spending less time on acquiring data form primary standards that do not provide optimal matrix matching.

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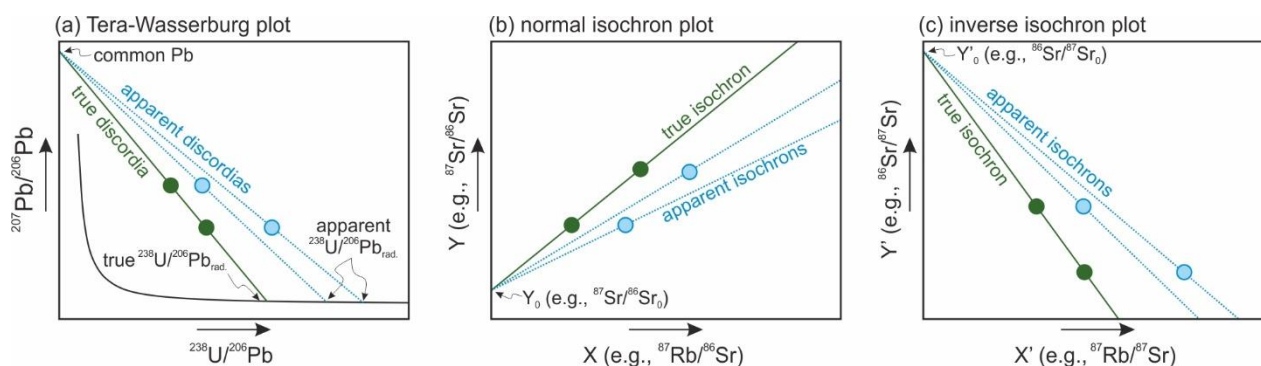


**Figure 1: Schematic illustrations for how individual analyses of primary standards with variable parent and daughter isotope concentrations can be used to obtain factors for elemental fractionation correction. (a) One of the approaches taken in U-Pb geochronological applications of LA-ICP-MS. Factors for U-Pb fractionation correction are calculated by rationing the true and apparent $^{238}U/^{206}Pb_{radiogenic}$ ratios that are obtained using the Tera-Wasserburg diagram. (b-c) Potential approaches for non-U-Pb geochronological applications of LA-ICP-MS. Factors for elemental fractionation correction can be estimated by finding coefficients by which the measured elemental ratios need to be multiplied to equate the slopes of the apparent and true isochrons, whether normal or inverse. Elemental fractionation correction factors can also be estimated by comparing the true and apparent intercepts with the horizontal axis in the inverse isochron diagram.**