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Corrigendum

Corrigendum to “Isotopic fractionation accompanying CO₂ hydroxylation and carbonate precipitation from high pH waters at the Cedars, California, USA” [Geochim. Cosmochim. Acta 301 (2021) 91–115]



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The authors regret that in the original article, the kinetic fractionation factors (KFFs) related to the CO₂ hydroxylation reaction (CO_{2(aq)} + OH⁻ → HCO₃⁻) were calculated using atmospheric δ¹⁸O_{CO₂ values of 0.0 ± 0.5 ‰ (VPDB) while the correct values are 10.25 ± 0.5 ‰ (VPDB). We erroneously employed the atmospheric δ¹⁸O_{CO₂ values from the NOAA CO₂ global network (Trolier et al., 1996) by not converting atmospheric δ¹⁸O_{CO₂ from the VPDB-CO₂ scale to the VPDB scale through the following expression (e.g. Srivastava and Verkouteren, 2018):}}}

$$\delta^{18}\text{O}_{\text{VPDB-CO}_2} = (\delta^{18}\text{O}_{\text{VPDB}} - 10.25)/1.01025. \quad (1)$$

This correction affects the reported oxygen isotope KFFs for CO₂ hydroxylation to form HCO₃⁻ prior to CaCO₃ precipitation. We have corrected Table 7 and Fig. 13 accordingly (see below). The composition of atmospheric CO₂ was also incorrectly plotted on the VPDB scale in Figs. 1, 8 and 15 of our original manuscript based on previous works (Fig. 8 in Clark and Fontes, 1990; Fig. 2 in Clark et al., 1992).

Importantly, the modelling outputs and main conclusions of the original article are not affected by these corrections. Nevertheless, the updated KFFs resolve an apparent discrepancy between the laboratory and field studies in our original article. Moreover, the oxygen isotope KFF for CO₂ hydroxylation now displays a positive temperature dependence over the 4–28 °C range, which was not statistically significant in the original article (Fig. 13c, r² = 0.86, n = 10, p-value <0.01):

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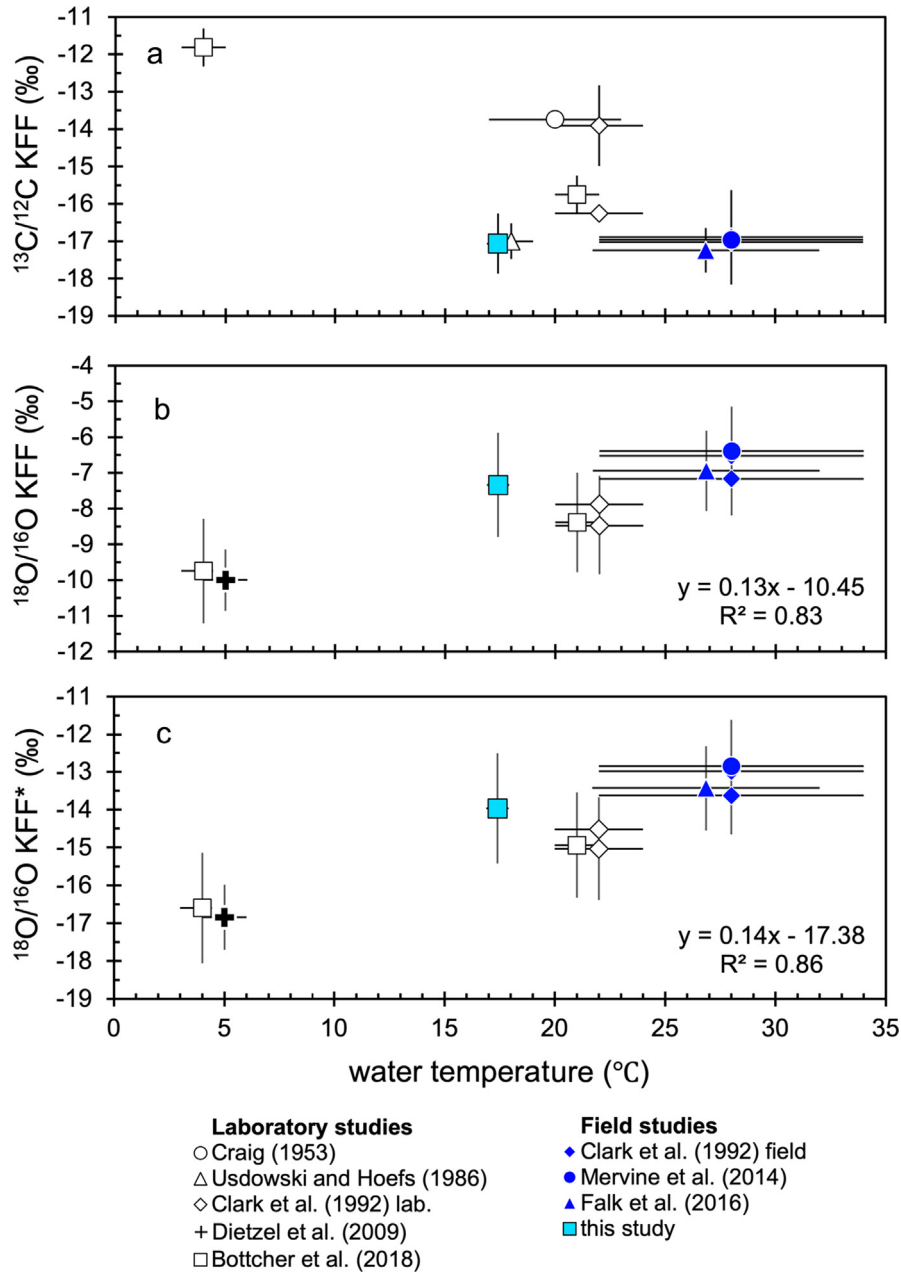


Fig. 13. Compilation of kinetic isotope fractionation factors (KFFs) related to the CO₂ hydroxylation reaction determined from laboratory and field studies. (A) Carbon KFF estimates showing a consistent cluster of field data at around -17.0 ± 0.3 ‰ and more scattered KFF estimates from laboratory studies. (B) Oxygen KFF estimates expressed relative to the weighted sum of reactants 'CO₂ + OH⁻'. (C) Oxygen KFF* estimates expressed relative to the weighted sum of 'CO₂ + H₂O'.

$$\text{KFF}^* (\text{‰}) = (0.14 \pm 0.02)T - 17.4 \pm 0.6, \quad (2)$$

where T is in °C, the uncertainty represents one standard error, and KFF* is the oxygen isotope kinetic fractionation factor between the HCO₃⁻ product and 'CO_{2(aq)} + H₂O' expressed as the per mil deviation from unity:

$$\text{KFF}^* = (\alpha_{\text{HCO}_3^-} / \alpha_{\text{CO}_2(\text{aq})} + \text{H}_2\text{O} - 1) 10^3. \quad (3)$$

Here and in the original article, the KFF is expressed relative to the weighted sum 'CO_{2(aq)} + H₂O' rather than 'CO_{2(aq)} + OH⁻' (i.e. the reactants) to avoid the uncertainty on the OH⁻-H₂O fractionation factor (Zeebe, 2020; Bajnai and Herwartz, 2021).

δ¹⁸O and oxygen KFF values in bold have been corrected by converting atmospheric δ¹⁸O_{CO₂} values from the VPDB-CO₂ scale to the VPDB scale using Eq. (1).

The authors apologize for any inconvenience caused.

Table 7
Compilation of CO₂ hydroxylation KFFs.

Reference	Study type	Mineral	T (°C)	±	pH	δ ¹³ C (‰ VPDB)				Carbon KFF		δ ¹⁸ O (‰ VSMOW)					Oxygen bulk KFF				
						CO _{2(g)}	±	Mineral	±	vs CO _{2(aq)} ^h	±	H ₂ O	±	CO _{2(g)}	±	Mineral	±	vs 'CO ₂ (aq) + OH ^{-k}	±	vs 'CO _{2(aq)} + H ₂ O' (KFF*)	±
Craig (1953)	Lab	Witherite	20	3	?	-9.1	0.1	-23.1	0.1	-13.7 ⁱ	0.1	-	-	-	-	-	-	-	-	-	-
Usdowski and Hoefs (1986)	Lab	Witherite	18	1	10.0	-7.7 ^a	0.3	-25.6	0.4	-17.0	0.5	-	-	-	-	-	-	-	-	-	-
Clark et al. (1992)	Lab	Witherite	22	2	> 11.5	-10.5	0.4	-25.0	1.0	-13.9 ⁱ	1.1	-6.7	0.1	36.6	0.3	6.8	1.0	-8.5	1.4	-15.0	0.2
Clark et al. (1992)	Lab	Witherite	22	2	12.8	-45.2	0.1	-61.3	0.1	-16.3 ⁱ	0.1	-11.9	0.1	11.1	0.1	-11.2	0.1	-7.9	0.8	-14.5	0.1
Dietzel et al. (2009)	Lab	Calcite	5	1	10.5	-	-	-	-	-	-	-9.6	0.1	35.7 ^j	0.1	3.4	0.1	-10.0	0.9	-16.8	0.1
Bottcher (2018)	Lab	Witherite	4	1	12.4	-8.6 ^b	0.5	-21.4	0.1	-11.8	0.5	-7.0	0.1	41.5 ^b	1.0	8.3	0.1	-9.7	1.5	-16.6	0.7
Bottcher (2018)	Lab	Witherite	21	1	12.4	-8.6 ^b	0.5	-25.3	0.1	-15.8	0.5	-7.0	0.1	41.5 ^b	1.0	10.0	0.1	-8.4	1.4	-14.9	0.7
Clark et al. (1992)	Field	Calcite	28	6	11.5	-7.5	1.1	-25.4 ^c	0.2	-17.0	1.1	-0.5	0.1	41.7 ^b	0.5	14.3 ^c	0.9	-6.5	1.4	-13.0	0.4
Clark et al. (1992)	Field	Calcite	28	6	11.5	-7.5	1.1	-25.3 ^d	0.7	-16.9	1.3	-0.9	0.1	41.7 ^b	0.5	13.5 ^d	0.1	-7.2	1.0	-13.6	0.4
Mervine et al. (2014)	Field	Calcite	28	6	11.0	-8.6 ^b	0.2	-26.5 ^e	0.3	-17.0	0.3	-0.5	1.5	41.7 ^b	0.5	14.4 ^e	0.4	-6.4	1.1	-12.9	0.8
Falk et al. (2016)	Field	Arag. & calcite	27	5	11.7	-8.6 ^b	0.2	-26.8 ^f	0.6	-17.2	0.6	0.1	1.0	41.7 ^b	0.5	14.0 ^f	0.4	-6.9	1.1	-13.4	0.7
This study	Field	Arag. & calcite	17	1	11.0	-8.6 ^b	0.4	-26.6 ^g	0.7	-17.1	0.8	-5.7	1.2	41.5 ^b	1.0	11.4 ^g	0.4	-7.3	1.5	-14.0	1.1

Note: KFFs are expressed as $\epsilon = (\alpha - 1)10^3$.

^a Keeling et al. (2001), station La Jolla (CA, USA).

^b NOAA CO₂ global network station closest to study site (incl. 2017 Ochsenkopf, Germany; 2007–2012 Ketura, Israel; 2007–2012 Kaashidhoo, Maldives; 2013–2018 Trinidad Head, USA).

^c Average modern crust 'NJ' samples.

^d Average modern crust 'clinic' samples.

^e Average of two lowest 'crust' samples.

^f Average of 'WHOI surface film' samples.

^g Average 'BSC floes' samples.

^h CO_{2(aq)}-CO_{2(g)} carbon fractionation of 1.1‰ from Vogel et al. (1970).

ⁱ Corrected for distillation effect.

^j CO₂-H₂O isotopic equilibrium assumed.

^k Calculated with OH⁻-H₂O EFF values from Zeebe (2020).

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