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Reply on Comment by Longinelli (2013) on a revised phosphate–water fractionation equation

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Longinelli (2013) contests the new phosphate–water oxygen isotope fractionation equation presented for fish teeth in Pucéat et al. (2010), and more specifically the pooling of the data of Pucéat et al. (2010) with those of Longinelli and Nuti (1973b), performed to better constrain the regression parameters of the fractionation equation.

Firstly, Longinelli (2013) criticizes that only 17 of the 24 data reported in Longinelli and Nuti (1973b) appear in Fig. 3. Doubt was cast on whether the fish data of Longinelli and Nuti (1973b) were mixed with those of marine molluscs from Longinelli and Nuti (1973a). Only oxygen isotope ratios of fish (Longinelli and Nuti, 1973b) have been taken into account in Pucéat et al. (2010), and all 24 data points were used for further calculation. The reason why only 17 samples are visible in Fig. 3 is that one data point (n° 18, following the sample identification of Longinelli and Nuti, 1973b) plots outside the scale of Fig. 3 of Pucéat et al. (2010), and that samples with identical oxygen isotope values plot on each other (n° 1, 8 and 9; n° 2 and 3; n° 4, 5 and 6; n° 12 and 15 following the sample identification of Longinelli and Nuti, 1973b). Fig. 1 shows all data points reported by Longinelli and Nuti (1973b) with the original sample identifications so that the reader will be able to identify easily every sample. The equation given in Fig. 3 is that reported in Longinelli and Nuti (1973b), originally published in Longinelli and Nuti (1973a), and shown for comparison.

Secondly, Longinelli (2013) questions the +2.2‰ correction that was performed on the data of Longinelli and Nuti (1973b) and Kolodny et al. (1983) before pooling these data (measured on $BiPO_4$) with ours (measured on Ag_3PO_4). Longinelli (2013) argues that the phosphate $\delta^{18}O$ values of Jurassic and Cretaceous belemnites measured using $BiPO_4$ (Longinelli and Nuti, 1968) and Ag_3PO_4 precipitations (Longinelli et al. 2002, 2003) plot in the same range, suggesting that both techniques yield comparable results. To our knowledge, the belemnite samples analyzed in 1968 are not the same specimens than those analyzed in 2002 and 2003, and for most of them, if not all, they have neither been recovered from the same stratigraphic levels nor from the same localities. This is problematic considering the secular fluctuations in $\delta^{18}O$ of marine hardparts that have been reported for the Jurassic and Cretaceous, both at longer and shorter time-scales, mainly resulting from paleotemperature variations (e.g. Huber et al., 1995; Steuber et al., 2005; Dera et al., 2011). Moreover, even in case analyses are available for belemnites from the same formation, the $\delta^{18}O$ values exhibit a quite large range (e.g. Toarcian: 5.7‰; Longinelli et al., 2002), that complicates any comparison based on a small number of samples. For all these reasons, it is very difficult if not impossible to make a statistical inference with such a dataset. Analyses of the same belemnite specimen with both the $BiPO_4$ and Ag_3PO_4 methods would be required to answer the question whether both methods result in comparable oxygen isotope ratios. As emphasized in Pucéat et al. (2010), such a comparison was already conducted by O'Neil et al. (1994) who analyzed

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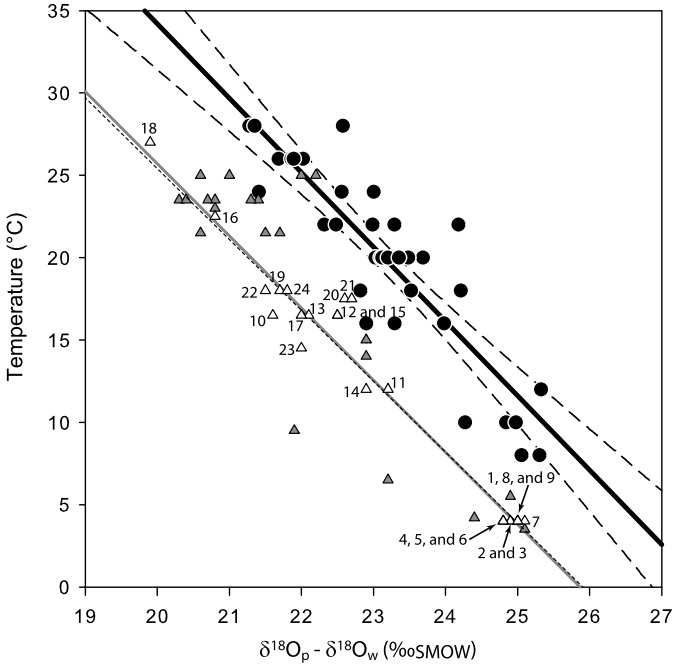

Fig. 1. Temperature versus $\delta^{18}O_p$–$\delta^{18}O_w$ for fish teeth measured in Pucéat et al. (2010) (black filled circle). Fish $\delta^{18}O$ values published by Longinelli and Nuti (1973b) and Kolodny et al. (1983) are shown as white and grey triangles, respectively. Black bold line represents the linear regression computed for the data of Pucéat et al. (2010), 95% confidence interval shown by long dashed lines. Regression analysis has been computed using the method implemented in R (http://www.r-project.org). Fractionation equations provided by Longinelli and Nuti (1973b), originally published in Longinelli and Nuti (1973a), and by Kolodny et al. (1983) are shown for comparison (black dotted line and grey line, respectively).

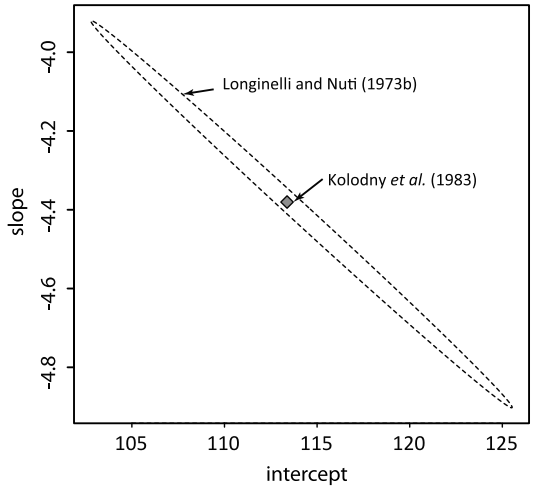

Fig. 2. Joint confidence area for the slope and intercept of the linear regression (95% confidence level) using the data of Longinelli and Nuti (1973b; black dashed ellipse), with the slope and intercept of the fractionation equation published in Kolodny et al. (1983) given as grey diamond. Joint confidence regions of estimates were computed with R using the ELLIPSE package, following an adapted version of the procedure described in Cornillon and Matzner-Løber (2007).

the $\delta^{18}O$ of 16 samples (enamel, bone, phosphorite) using Ag_3PO_4 precipitation, for which $\delta^{18}O$ values acquired using $BiPO_4$ precipitation had been published. A unilateral t-test for paired data confirms that $\delta^{18}O$ values obtained on Ag_3PO_4 are significantly higher than those measured using the $BiPO_4$ method ($t = 4.73$, $p = 10^{-4}$). The same result is found applying a less constraining non-parametric test, i.e. a Wilcoxon signed rank test for paired data ($V = 129.5$, $p < 10^{-3}$).

As noted by Longinelli (2013), a major concern of the bismuth phosphate method is the hygroscopicity of $BiPO_4$ and the removal of water before fluorination of $BiPO_4$. $BiPO_4$ should be heated in vacuo to at least 420 °C (Kahru and Epstein, 1986) to prevent bismuth phosphate from rehydration. Heating to lower temperatures may result in a relatively fast rehydration as observed by Kahru and Epstein (1986). Those authors stated that the procedures of Longinelli (1965) and Kolodny et al. (1983) did not adequately remove the water of hydration prior to fluorination, and that their data may be biased towards lower $\delta^{18}O$ values (p. 1747). Kolodny et al. (1983) heated the $BiPO_4$ samples only to 100 °C. Longinelli and Nuti (1973a, 1973b) did not provide detailed information on the procedure of $BiPO_4$ precipitation but refer to the method of Tudge (1960) with bismuth phosphate heated to 140 °C. We acknowledge that later $BiPO_4$ precipitates may have been heated to higher temperatures (e.g. Delgado Huertas et al., 1995) and thus give correct oxygen isotope values. However, as previously shown by O'Neil et al. (1994), Fox and Fisher (2001) and Chenery et al. (2010), we argue that a correction of earlier oxygen isotope analyses on bismuth phosphate is required, most probably due to the insufficient heating of the bismuth phosphate samples.

It is difficult to estimate the exact value of the correction based on the data of Longinelli and Nuti (1973b), as to our knowledge, the authors did not analyze NBS120b with the $BiPO_4$ technique. By contrast, comparison of the $\delta^{18}O$ value of NBS120b (20.0‰ on average; Shemesh et al., 1988; Bryant et al., 1994) analyzed using the same laboratory and technique than in Kolodny et al. (1983) with that measured in Pucéat et al. (2010; NBS120b = 22.2‰) highlights an offset of 2.2‰. The regression parameters of the equation from Kolodny et al. (1983) are included in the ellipse representing the confidence region of the regression estimates defined by the data from Longinelli and Nuti (1973b) (Fig. 2). Thus, both equations are not statistically different. This suggests that the data from Longinelli and Nuti (1973b) need to be corrected by +2.2‰ as well. Note that if only the data of Kolodny et al. (1983) corrected by +2.2‰ are pooled with the data of Pucéat et al. (2010), the temperature equation would be the same than the one published in Pucéat et al. (2010), with the same slope and an insignificant difference for the intercept (118.6 vs 118.7). Therefore, we argue that the equation published in Pucéat et al. (2010) does not require any correction, even if the data of Longinelli and Nuti (1973b) are not considered for the pooling. This of course does not rule out another revision of the temperature equation to become necessary in the future, for example as consequence of the progressive availability and increasing use of certified reference materials, as has occurred since the pioneering studies of A. Longinelli and Y. Kolodny.

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