

**Authors' response to "Interactive comment on "The oxygen isotopic composition of phytoliths from tropical rainforest soils (Queensland, Australia): application of a new paleoenvironmental tool" by Anonymous Referees #1 and #2.**

The authors want to thank anonymous referees #1 and #2 for their detailed and constructive reviews. Both reviewers points out the lack of measured climate,  $\delta^{18}\text{O}_{\text{precipitation}}$  and  $\delta^{18}\text{O}_{\text{soil}}$  data, and advice to introduce a more detailed discussion of the various unknowns. In agreement with these comments we further discuss those unknowns and carefully assess uncertainties associated with i)  $\delta^{18}\text{O}_{\text{precipitation}}$ , MAP and MAT estimates and ii)  $\delta^{18}\text{O}_{\text{silica}}$  and  $\delta^{18}\text{O}_{\text{wood phytolith}}$  estimates (as presented below).

However, we first would like to make clear that the aim of our study was not to introduce an additional phytolith-water fractionation curve. For this purpose and ideally, matching the 100s years time span recorded by the soil phytolith assemblages would have required to obtain, for each of the sampled sites, mean values (at least over 10s of years) for MAT,  $\delta^{18}\text{O}_{\text{soil water}}$  and/or  $\delta^{18}\text{O}_{\text{precipitation}}$ , which was unrealistic. Another option would have been to measure  $\delta^{18}\text{O}$  signature of wood phytoliths grown over several years under controlled conditions of temperature and  $\delta^{18}\text{O}_{\text{soil water}}$ . However, with the aim of palaeoenvironmental reconstructions, one has to keep in mind that the majority of phytoliths found in sediments come from the soil tops. Application of a relationship obtained from cultivated wood phytoliths to soil and sediment phytolith assemblages would have not been straightforward due to i) the heterogeneity of phytolith productivity from a tree species to another and ii) selective phytolith dissolution in litter and soil (Alexandre et al.,1997). Instead, our aim was rather to check whether, under natural rainforest conditions, changes in  $\delta^{18}\text{O}$  of soil phytolith assemblages (dominated by wood phytoliths) were reflecting changes in MAT and  $\delta^{18}\text{O}_{\text{precipitation}}$  in the range predicted by equilibrium temperature coefficients previously published for the different silica-water couples. In order to limit the uncertainty associated with  $\delta^{18}\text{O}_{\text{precipitation}}$  estimates, we deliberately choose to sample 17 sites along 4 altitude gradients that are close to each other by less than 100km, receive their precipitation from similar air masses (brought by the dominant NW monsoonal winds), are similarly characterized by podzolic soils developed at the expense of granitic and metamorphic parent-rocks, and are all (except site 21) covered by a closed rainforest with a very low range of vapor pressure deficit for much of the time (0-0.2kPa; Hutley et al., 1997). For this samples set, altitude is the main control on temperature ( $R^2=0.97$ , calculated from Table 1 of the CPD manuscript) and we reasonably assume that the cumulative difference of altitude crossed by the dominant S-E trade winds is the main control on  $\delta^{18}\text{O}_{\text{precipitation}}$  values ( $R^2 = 0.9$ ; calculated from Table 1). This approach will be explained with more clarity in a revised manuscript.

**Detailed answers to major comments from referee #1 are presented below ("minor" comments will be taken into account in the revised manuscript).**

*Title* will be modified according to the reviewer's suggestion as "The oxygen isotopic composition of phytolith assemblages from tropical rainforest soil tops (Queensland, Australia): validation of a new paleoenvironmental tool"

*Estimation of changes in  $\delta^{18}\text{O}_{\text{precipitation}}$  values : rationale and uncertainty* – We used as a basis the Bowen and Wilkinson (2002) equations (eq 5 and 6 in the CPD manuscript) where  $\delta^{18}\text{O}_{\text{precipitation}}$  values are controlled by the latitude and by the latitude-independent effect of altitude. Furthermore, in order to take into account the cumulative rainout (Lachniet and Patterson, 2009), especially at leeward sites, the cumulative difference of the altitude crossed by the dominant S-E trade winds before reaching the sampled sites ( $|\Delta\text{ALT}|$ ) was used instead of  $|\text{ALT}|$  for estimating  $\delta^{18}\text{O}_{\text{precipitation}}$  (eq. 7 and 8). Additionally, in the light of the few isotopic studies investigating the water cycle in other rainforest areas, which found an inland  $^{18}\text{O}$  gradient of  $-0.08\text{‰}/100\text{km}$  reflecting the influence of recycled continental moisture (mainly from evapo-transpiration) (Salati et al., 1979; Gat & Matsui, 1991; Martinelli et al., 1996; Njitchoua et al., 1999; Lachniet and Patterson, 2002), the inland  $^{18}\text{O}$  gradient term ( $-0.08$  (DIST)) was added (eq. 7 and 8). However, given the sites proximity to the coast, the inland gradient has no significant impact on  $\delta^{18}\text{O}_{\text{precipitation}}$  values. Finally, because the sites are close to each other (similar or close latitude), the latitude-independent altitude effect is discriminatory. It was calculated by Bowen and Wilkinson (2002) as  $0.002\text{‰}/\text{m}$  a.s.l. (the slope of the relationship calculated by Bowen and Wilkinson (2002) has a standard error of  $0.0002\text{‰}/\text{m}$  and is highly significant at the 95% confidence level ( $p= 0.0001$ )). The magnitude of the altitude effect was also measured worldwide (Chamberlain and Poage, 2000 : the slope of the best fit line is  $0.0021\text{‰}/\text{m}$  ( $R2 = 0.79$ ); Gonfiantini *et al.*, 2001; Lachniet and Patterson, 2002 : the slope of the best fit line is  $0.0019\text{‰}/\text{m}$  ( $R2 = 0.89$ ); Lachniet and Patterson, 2009: the slope of the best fit line is  $0.0025\text{‰}/\text{m}$  ( $R2 = 0.72$ )). From these data an uncertainty lower than  $\pm 0.0005\text{‰}/\text{m}$  can be reasonably associated with the  $0.002\text{‰}/\text{m}$  a.s.l. altitude effect. Uncertainty associated with the latitude parameter in eq. 7 and 8 is not known but is similar for all the sites. At the global scale, the average difference between  $\delta^{18}\text{O}_{\text{precipitation}}$  values estimated from eq. 5 and 6 (including an altitude parameter) and the measured values is  $0.21\text{‰}$  ( $\sigma= 2.49\text{‰}$ ) (Bowen and Wilkinson, 2002). Added to the altitude effect uncertainty estimated above, it leads to a propagated uncertainty on  $\delta^{18}\text{O}_{\text{precipitation}}$  estimates ranging from 0.2 to 0.8 ‰ for Palmerston, Mt Edith and Northern Cairns sites and from 0.8 to 1.2‰ for Bartle Frere transect. Following reviewer #1 suggestions, those uncertainties are now properly defined and displayed in an additional column in Supplementary material: table 1.

As previously wrote in the CPD manuscript, differences between estimated weighted mean annual  $\text{d}^{18}\text{O}_{\text{precipitation}}$  values (eq.7 and 8) and measured weighted mean seasonal  $\text{d}^{18}\text{O}_{\text{precipitation}}$  values obtained by the CSIRO Land and Water during two rainy seasons in 1998 and 1999 for two stations of the Atherton Tableland (Malanda and Walkamine; those were the only data available for the area) were very small (respectively  $+0.18$  and  $-0.08\text{‰}$ ). This comparison strengthened the reliability of the  $\delta^{18}\text{O}_{\text{precipitation}}$  estimations from eq. 7 and 8.

*Corrections on  $\delta^{18}\text{O}_{\text{silica}}$  and  $\delta^{18}\text{O}_{\text{wood phytolith}}$ : uncertainties* – We now estimate, for each of the samples, the mean and standard deviation (SD) of X (exchangeable oxygen),  $\delta^{18}\text{O}_{\text{silica}}$ , and corrected  $\delta^{18}\text{O}_{\text{silica}}$  using R and a Monte Carlo simulation (Supplementary material: table 2). X,  $\delta^{18}\text{O}_{\text{silica}}$  and corrected  $\delta^{18}\text{O}_{\text{silica}}$  were computed 10 000 times, using 10 000 simulated values of the variables taken into account in the equations (Crespin et al., 2008 and section 4.3 of the CPD manuscript). The simulated uncertainty (SD) on corrected  $\delta^{18}\text{O}_{\text{silica}}$  ranges from  $\pm 0.5$  to  $1.5\text{‰}$  for 16 over 17 samples and is  $2.7\text{‰}$  for S38 (Supplementary material: table 2). Given a counting error of  $\pm 3.5\%$  (SD), the uncertainty on  $\delta^{18}\text{O}_{\text{wood phytolith}}$  due to the quartz weight correction ranges from 0.5 to  $0.9\text{‰}$  for the 7 samples where

some quartz particles were counted. Finally the propagated uncertainty (SD) on  $\delta^{18}\text{O}_{\text{wood phytolith}}$  range from 0.8 to 1.5‰ for 16 over 17 samples and is 2.7‰ for S38 (Supplementary material: table 2; Figure 1).

*Uncertainty associated with  $[\Delta^{18}\text{O}_{\text{wood phytolith-precipitation}}]$*  – Given the uncertainties on  $\delta^{18}\text{O}_{\text{wood phytolith}}$  and  $\delta^{18}\text{O}_{\text{precipitation}}$ , the propagated uncertainties on  $\Delta^{18}\text{O}_{\text{wood phytolith-precipitation}}$  range from 0.8 to 1.6‰ for 15 over 17 samples and is 2.9 and 1.8‰ for S38 and S37 respectively (Supplementary material: Table 2; Figure 2).

*Uncertainties associated with MAP and MAT estimates* - Making due allowance for varying conditions, station density and standardisation to 30 years, the predictive errors in MAP from the ANUCLIM surfaces are around 10-15% across the continent (Hutchinson, personal communication; Hutchinson, 1991; Hutchinson, 1995). For MAT, given the standard errors in monthly max and min of no more than 0.5°C, a standard error of around 0.2°C would be a conservative estimate (Hutchinson, personal communication; Hutchinson, 1991; Hutchinson, 1995) (Supplementary material: table 2; Figure 1)

*Possible influence of soil evaporation and groundwater on  $\delta^{18}\text{O}_{\text{soil water}}$*  - As previously explained in the CPD manuscript (section 4.6) because Australian rainforests are characterized by low radiation levels due to frequent occurrence of fog and low clouds and a very low range of the vapor pressure deficit (0-0.2kPa; Hutley et al., 1997) for much of the time, soil evaporation and understorey evaporation are expected to be low (Hutley et al., 1997). For comparison, in the Amazonian rainforest, calculated soil evaporation is less than 0.5% of the total evapo-transpiration while transpiration and interception evaporation represents respectively 79 and 20% of the total evapo-transpiration (Ashbi, 1999). Another study demonstrated that  $\delta^{18}\text{O}_{\text{soil water}}$  values measured in the Amazonian rainforest were close to  $\delta^{18}\text{O}_{\text{precipitation}}$  values and lie along the local isotopic meteoric water line (Girard *et al.*, 2000). However there are indeed no available measurements from the Australian rainforests, and we are not aware of any reliable way of estimating rainforest soil evaporation (and more generally evaporation from non bare soils) from climate data only (without taking into account soil and canopy parameters). We would be very glad to get a reference on that subject.

The poorly drained podzolic soils are mainly developed at the expense of granitic and metamorphic parent- rocks. The sites are mainly located on steep slopes and shallow groundwater may locally occur at the boundary between arenite and soils. In this case, groundwater will rather get a local  $\delta^{18}\text{O}$  signature that should not impact the long term  $\delta^{18}\text{O}_{\text{soil water}}$  signature.

*Over 600 years a good deal of climate variability has occurred. How does such variability effect the interpretation?*

- This was previously discussed in the CPD manuscript (section 4.6): “Ideally, matching the time span recorded by the soil phytolith assemblages would require us to obtain, for each of the sampled sites, measurements for 100s of years for MAT,  $\delta^{18}\text{O}_{\text{soil water}}$  and/or  $\delta^{18}\text{O}_{\text{precipitation}}$  values, which is unrealistic”... “Regarding atmospheric temperature, measurements back to 1910 revealed a fast increase of MAT of +0.1°C/10y, mostly during the second half of the 19<sup>th</sup> century in Queensland (Suppiah et al., 2001). To our knowledge there is no other continuous record of temperature from any tropical Australian site. A dendroclimatological study showed evidence of a much slower increasing trend of +1.5°C since the 16<sup>th</sup> century in New Zealand (Cook et al., 2002). From these records, the

assumption was made that modern long term MAT values extracted from the ANUCLIM database should only slightly overestimate (by less than 1-2°C) the mean value for the last 100s of years; this in a similar way for all the sampled sites.”

*What effect does a summer weighting have on the final temperature-fractionation plot?* - As previously stated in the CPD manuscript (section 4.6), we assumed that weighted mean seasonal values were close to the weighted mean annual values, since most of the precipitation occurs during the rainy season. This assumption was supported when comparing for Malenda and Walkamine stations, measured weighted mean seasonal  $\delta^{18}\text{O}_{\text{precipitation}}$  values and weighted mean annual  $\delta^{18}\text{O}_{\text{precipitation}}$  estimates.

**Detailed answers to major comments from referee #2 are presented below. We will carefully take into account “major” and “minor” comments in a revised manuscript.**

*“Tropical rainforests from Queensland are non-evaporative”*. Justify this statement. cf answer to reviewer 1.

*Temporal signal brought by soil phytolith assemblages; relevance of the comparison with mean annual data* - As written in the CPD manuscript (section 1), mean age of 100s of years was measured for bulk organic matter (OM) from one of the soil top samples investigated in the present study, and can be reasonably expected for phytoliths. Regarding atmospheric temperature, measurements back to 1910 revealed a fast increase of MAT of +0.1°C/10y, mostly during the second half of the 19<sup>th</sup> century in Queensland (Suppiah et al., 2001). To our knowledge there is no other continuous record of temperature from any tropical Australian site. A dendroclimatological study showed evidence of a much slower increasing trend of +1.5°C since the 16<sup>th</sup> century in New Zealand (Cook et al., 2002). From these records, the assumption was made that modern long term MAT values extracted from the ANUCLIM database should only slightly overestimate (by less than 1-2°C) the mean value for the last 100s of years; this in a similar way for all the sampled sites.

*Impact for future paleoenvironmental studies*- As underlined in section 1 of the CPD manuscript, “ 1) in small lake’s catchments covered by rainforest such as the ones found in Queensland (e.g. Haberle, 2005; Kershaw et al., 2007), phytoliths from eroded soil tops are expected to constitute the main source of fossil phytoliths in sediments; 2) the weak concentration of phytoliths in rainforest soil tops (a few ‰ in weight, Alexandre et al., 1997) and in the suspended load of tropical rivers (less than 5‰ in weight, Carry et al., 2005) suggests that the mean phytolith concentration in lake sediments is also on the order of a few ‰ in weight. Taking into account the amount of phytoliths required for  $\delta^{18}\text{O}$  analyses (several mg) and using the lake sediment accumulation rates commonly observed in Queensland rainforest environments (cm/100yrs; e.g. Haberle, 2005; Rieser and Wust, 2010), the fossil phytolith assemblages provided using sampling intervals of several centimeters in lake sediment cores should encompass 100s of years”, similarly to soil phytolith assemblages investigated here.

As assessed in the CPD manuscript (section 6.3 Implications for paleoenvironmental reconstructions) “... given the low amount of phytoliths recovered from soils and sediments, we expect the time resolution from sedimentary phytolith records to be limited to 100s yrs. However, such low uncertainty and time resolution are still sufficient for investigating significant terrestrial changes that occurred during the Quaternary glacial/interglacial transitions.”

*Soil phytolith assemblages: 80% of the phytoliths are “Globular granulate”, can more information be provided as to what the remaining 20% are?* Except from wood phytoliths there are palm, grass, and unclassified phytolith categories (that may originate from trees). This is presented in the result section (section 5.1 Phytolith assemblages) and in Table 2 of the CPD manuscript.

*MSG40 is used here as a phytolith standard. Crespin et al (2008) has previously provided a value of +38.4‰ for this standard, however the recent inter-lab calibration paper of Chaplignin (2011) now provides a value of +37.0‰. Please state which value has been used in this study.* In Chaplignin et al. (2011), MSG 60 (corrected  $\delta^{18}\text{O}_{\text{silica}}$  value of 36.9‰, pooled  $\delta^{18}\text{O}_{\text{silica}}$  value of 37.0‰) instead of MSG 40 was measured. In the frame of the present study and in a first step, one to three aliquots of a phytolith lab standard, MSG 40 (Crespin et al., 2008), were run per measurement session in order to verify the effectiveness of the CIE procedure: we checked that measured values of MSG 40 were always in the standard deviation of the mean value measured during the long term calibration published by Crespin et al. (2008) for MSG 40 ( $\delta^{18}\text{O}_{\text{measured } 1} = 36.67 \pm 0.36\%$ ;  $\delta^{18}\text{O}_{\text{measured } 2} = 39.00 \pm 0.36\%$ ). These measured values lead to a corrected  $\delta^{18}\text{O}_{\text{silica}}$  value of 37.3‰, which is not used for any correction. In a second step, the measured  $\delta^{18}\text{O}$  values of each sample ( $\delta^{18}\text{O}_{\text{measured } 1}$ ,  $\delta^{18}\text{O}_{\text{measured } 2}$ ) were corrected on a daily basis using a quartz lab standard ( $\delta^{18}\text{O}_{\text{Boulangé } 50-100 \mu\text{m}} = 16.36 \pm 0.09\%$ ). This will be made clearer in a revised manuscript.

*Concerns over the accuracy of the  $\delta^{18}\text{O}$  isotope data: Correction for the CIE offset: explanation* – The offset will be further explained in the revised manuscript as follow: The recent inter-laboratory comparison for oxygen isotopic composition of hydrous biogenic silica has evidenced that, when the CEREGE CIE is performed, a methodological bias occurs leading to abnormally high fractionation between the vapour and the exchanged oxygen ( $\Delta^{18}\text{O}_{\text{vapour-Oexchanged}}$ ) (Chaplignin et al., 2011). Tests were conducted to examine any possibility of systematic error: before the start of the CIE, the working standards were heated at 350°C in order to remove possible labile organic remains that may increase the surface area of the materials; the amount of silica subjected to exchange was increased by 6; water-vapour exchange temperature (and associated fractionation factor) was changed; time of vapour-silica exchange was increased while the volume of exchange was reduced by 1/3; the rate of silica dehydration was reduced. None of these tests produced significant changes in the  $\delta^{18}\text{O}_{\text{measured}}$  values. The difference between the two labelled waters was reduced by 8‰ which did not change the  $\delta^{18}\text{O}_{\text{silica}}$  values. Additionally, for two working standards (MSG60, BFC), vapour-silica exchanges were carried out at three temperatures (140°C, 200°C (usual temperature) and 246°C). Changes in  $\delta^{18}\text{O}_{\text{measured}}$  values were the ones expected from the temperature-dependency of the equilibrium fractionation factors  $\alpha_{\text{water-vapour}}$  and  $\alpha_{\text{vapour-exchanged}}$ . The methodological bias assumed to occur during vapour-silica exchange, remains unexplained but is however reproducible and can be quantified. For this purpose, pooled values obtained for the whole set of working standards (except NFC) (Chaplignin et al., 2011) were taken as true values. CEREGE 1000  $\ln \alpha_{\text{vapour-Oexchanged}}$  values obtained for 140 and 200° were compared to 1000  $\ln \alpha_{\text{vapour-Oexchanged}}$  values previously obtained for the same temperatures by Labeyrie and Juillet (1982). Differences were invariant with temperature and did not show any relationship with the measured percentage of exchangeable oxygen ( $R^2 = 0.08$ ) but decreased with increasing  $\delta^{18}\text{O}_{\text{silica}}$  values ( $R^2 = 0.4$  and 0.9 after outlier removal) (Figure 3).

In a first step, the empirical relationship was used to correct the values of  $\Delta_{\text{vapour-Oexchanged @ CEREGE}}$  ( $\Delta_{\text{vapour-Oexchanged}}$  was assumed similar to  $1000 \ln \alpha$ ) as follows:

$$\text{Corrected } \Delta_{\text{vapour-Oexchanged @ CEREGE}} = \Delta_{\text{vapour-Oexchanged from Labeyrie and Juillet (1982)}} - 1.3 * \delta^{18}\text{O}_{\text{silica @ CEREGE}} + 78$$

In a second step, the corrected  $\Delta_{\text{vapour-Oexchanged}}$  values were used to correct the  $\delta^{18}\text{O}_{\text{silica}}$  values.

Differences between corrected  $\delta^{18}\text{O}_{\text{silica}}$  and the pooled  $\delta^{18}\text{O}_{\text{silica}}$  values (HT with high Al and Fe contents, and NFC which over-reacted under the laser beam were not taken into account) still increase, from  $-0.1\text{‰}$  (MSG60) to  $+2.9\text{‰}$  (G95), with the content in total organic carbon (TOC; measured in Chaplignin et al., 2011) ( $R^2 = 0.8$  and  $0.9$ , respectively) (Figure 4). This relationship suggests that organic remains increase the CEREGE abnormally high fractionation between the vapour and the exchanged oxygen ( $\Delta^{18}\text{O}_{\text{vapour-Oexchanged}}$ ), which is not taken into account in the methodological bias correction.

Back to the Queensland rainforests samples, if the 6 samples where few organic matter particles were counted (Table 2) are removed from the samples set, the obtained relationship between [ $\Delta^{18}\text{O}_{\text{wood phytolith-precipitation}}$ ] and temperature becomes  $\Delta^{18}\text{O}_{\text{wood phytolith-precipitation}} = -0.34 t + 45$  which is still in the uncertainty of (eq. 12):  $\Delta^{18}\text{O}_{\text{wood phytolith-precipitation}} = -0.4 (\pm 0.2) t + 46 (\pm 3)$ .

*Concerns over the accuracy of the  $\delta^{18}\text{O}$  isotope data: correction for the presence of quartz, grass and palm phytoliths* – Table 3 may have lead to some confusion here and will be modified in a revised version of the manuscript. Correction for the presence of non-wood phytoliths does not significantly impact the obtained temperature-dependant relationship. As presented in the CPD manuscript (section 5.3 and section 6.) “Whether corrections for the presence of quartz particles, grass and palm phytoliths are made or not on  $\delta^{18}\text{O}_{\text{silica}}$  values,  $\Delta^{18}\text{O}_{\text{wood phytolith-precipitation}}$  values obtained for the windward transects showed close negative linear relationships with MAT expressed by their mean temperature coefficients ranging from  $-0.4$  to  $-0.5 (\pm 0.2) \text{‰}/^\circ\text{C}$  and their y-intercept ranging from  $46$  to  $48 (\pm 4) \text{‰}$ . These similarities showed the weak influence of the corrections for non-wood phytoliths on  $\delta^{18}\text{O}$  values of rainforest phytolith assemblages.”

*Concerns over the accuracy of the  $\delta^{18}\text{O}$  isotope data: propagation of errors* - Uncertainty associated with the methodological bias correction is now taken into account when mean and standard deviation (SD) of corrected  $\delta^{18}\text{O}_{\text{silica}}$  are calculated using a Monte Carlo simulation (cf Answer to reviewer 1 and Supplementary material: table 2). Propagated uncertainties on  $\delta^{18}\text{O}_{\text{wood phytolith}}$  range from  $\pm 0.8$  to  $\pm 1.5\text{‰}$  for 16 over 17 samples and is  $\pm 2.7\text{‰}$  for S38. Propagated uncertainties on  $\Delta^{18}\text{O}_{\text{wood phytolith-precipitation}}$  range from  $\pm 0.8$  to  $\pm 1.8\text{‰}$  for 16 over 17 samples and is  $\pm 2.9\text{‰}$  for S38 (Supplementary material: table 2; Figure 1; Figure 2).

*Concerns over the accuracy of the  $\delta^{18}\text{O}$  isotope data: is the G95-25-CL standard comprised of fresh phytoliths likely to be the closest match to the samples analysed in this paper ?* - The following points suggest that the investigated soil top phytolith assemblages do not get the same physical characteristics as the G95-25-CL standard made of fresh phytoliths from harvested grasses: 1) as presented in the CPD manuscript mean ages of the soil top phytolith assemblages are assumed to be in the order of 100s yrs and were already subjected to selective dissolution (Alexandre et al., 1997); 2) given the morphology of grass and wood phytoliths, surface area of grass phytoliths is

likely to be higher than the one of wood phytoliths (Alexandre et al., 2011), which would explain why grass phytoliths usually decrease with depth in tropical soils (Alexandre et al., 1997; Alexandre et al., 2011); 3) G95-25-CL standard contain 0.5% wt of carbon which may increase abnormally high fractionation between the vapour and the exchanged oxygen during the CEREGE CIE as previously suggested.

*Concerns over the accuracy of the  $\delta^{18}\text{O}$  isotope data - why is the quartz  $\delta^{18}\text{O}$  value of 8‰ used?* – the value of 8‰ was used for quartz particles as it is in the lower range of  $\delta^{18}\text{O}$  values measured worldwide for detrital quartz of metamorphic origin (e.g. Garlick and Epstein, 1967; Savin and Epstein, 1970; Clayton et al., 1972; Eslinger et al., 1973; Blatt, 1986; Graham et al., 1996 ; Alexandre et al., 2006).

*Concerns over the accuracy of the  $\delta^{18}\text{O}$  isotope data – Why were  $\delta^{18}\text{O}_{\text{soil water}}$  and  $\delta^{18}\text{O}_{\text{precipitation}}$  not directly measured in the field?:* As presented in section 4.6 of the CPD manuscript: “Ideally, matching the time span recorded by the soil phytolith assemblages would require us to obtain, for each of the sampled sites, measurements for 100s of years for MAT,  $\delta^{18}\text{O}_{\text{soil water}}$  and/or  $\delta^{18}\text{O}_{\text{precipitation}}$  values, which is unrealistic...” In the absence of long term (10s of years)  $\delta^{18}\text{O}_{\text{precipitation}}$  and/or  $\delta^{18}\text{O}_{\text{soil water}}$  measurements from Queensland rainforests, assumption was made that the long term depth-weighted  $\delta^{18}\text{O}_{\text{soil water}}$  values average the long term amount-weight mean annual  $\delta^{18}\text{O}_{\text{precipitation}}$  values. Those were estimated using as a basis the relationships established by Bowen and Wilkinson (2002) from long term data obtained from the International Atomic Energy Agency-World Meteorological Organization Global Network for Isotopes in Precipitation (GNIP) database (IAEA/WMO, 1998).

*Dissolution of phytoliths in soils and associated fractionation* – As presented in section 6.1 of the CPD manuscript phytolith dissolution may indeed explain the relative shift of the obtained temperature-dependant relationship to the one previously obtained for harvested grass phytoliths (Shahack-Gross et al., 1996) : “At least, superficial dissolution of phytoliths in litter and soil (Alexandre et al., 1999) may also lead to slight  $^{18}\text{O}$  enrichment as the lighter isotope, forming weaker bonds and having a higher diffusion velocity than the heavier isotope, goes preferentially to the liquid phase. Dissolution figures are difficult to detect on the granulated surface of the globular granulate phytolith type which prevents verifying the later hypothesis.”

## References

- Alexandre, A., Meunier J.D., Colin F. Koud J.M. (1997). Plant impact on the biogeochemical cycle of silicon and related weathering processes. *Geochimica et Cosmochimica Acta* 61(3): 677-682.
- Alexandre, A., I. Basile-Doelsch, et al. (2006). "Oxygen isotope analyses of fine silica grains using laser-extraction technique: Comparison with oxygen isotope data obtained from ion microprobe analyses and application to quartzite and silcrete cement investigation." *Geochimica et Cosmochimica Acta* 70(11): 2827-2835.
- Alexandre, A., M. Bouvet, et al. (2011). "The role of savannas in the terrestrial Si cycle: A case-study from Lamto, Ivory Coast." *Global and Planetary Change* 78: 162–169.
- Ashby, M. (1999), Modelling the water and energy balances of Amazonian rainforest and pasture using Anglo-Brazilian Amazonian climate observation study data, *Agricultural and Forest Meteorology*, 94(2), 79-101.
- Blatt, H., 1986. Oxygen isotopes and the origin of quartz. *J. Sediment. Petrol.* 57, 373–377.
- Bowen G.J. and Wilkinson B. (2002) Spatial distribution of  $\delta^{18}\text{O}$  in meteoric precipitation. *Geology* 30(4), 315-318.
- Cary L., Alexandre A., Meunier J.D., Boeglin J.L. and Braun J.J. (2005) Contribution of phytoliths to the suspended load of biogenic silica in the Nyong basin rivers (Cameroon). *Biogeochemistr.* 74, 101-114.
- Chamberlain, C. P., and M. A. Poage (2000), Reconstructing the paleotopography of mountain belts from the isotopic composition of authigenic minerals, *Geology*, 28(2), 115-118.
- Chapligin B., Leng M.J., et al. 2011. "Inter-laboratory comparison of oxygen isotopes from biogenic silica." *Geochimica et Cosmochimica Acta*. In Press.
- Clayton, R.N., O'Neil, J.R., Mayeda, T.K., 1972. Oxygen isotope exchange between quartz and water. *J. Phys. Res.* 77, 3057–3067.

- Cook E.R., Palmer J.G., D'Arrigo R.D. (2002) Evidence for a 'Medieval Warm Period' in a 1,100 year tree-ring reconstruction of past austral summer temperatures in New Zealand. *Geophys. Res. Lett.*, 29-14, 10.1029/2001GL014580.
- Crespin, J., A. Alexandre, et al. (2008) "IR laser extraction technique applied to oxygen isotope analysis of small biogenic silica samples." *Analytical Chemistry*. 80(7): 2372-2378.
- Eslinger, E., Mayer, L.M., Durst, T.L., Hower, J., Savin, S.M. (1973). An X-ray technique for distinguishing between detrital and secondary quartz in the fine-grained fraction of sedimentary rocks. *J. Sediment. Petrol.* 43, 540-543.
- Garlick, G.D., Epstein, S. (1967). Oxygen isotope ratios in coexisting minerals of regionally metamorphosed rocks. *Geochim. Cosmochim. Acta* 31, 181-214.
- Gat, J. R., and Matsui, E. (1991) Atmospheric water balance in the Amazon basin: An isotopic evapotranspiration model. *J. Geophys. Res.*, 96 (D7) 13179-13188.
- Graham, C.M., Valley, J.W., Winter, B.L. (1996) Ion microprobe analysis of  $^{18}\text{O}/^{16}\text{O}$  in authigenic and detrital quartz in the St. Peter Sandstone, Michigan Basin and Wisconsin Arch, USA contrasting diagenetic histories. *Geochim. Cosmochim. Acta* 60, 5101-5116.
- Girard J.P., Freyssinet P., and Chazot G. (2000) Unraveling climatic changes from intraprofile variation in oxygen and hydrogen isotopic composition of goethite and kaolinite in laterites: an integrated study from Yaou, French Guiana. *Geochim. Cosmochim. Acta* 64(3), 409-426.
- Gonfiantini R., Roche M.A., Olivry J.C., Fontes J.C., Zuppi G.M. (2001) The altitude effect on the isotopic composition of tropical rains. *Chem. Geol.* 181, 147-167.
- Haberle S.G. (2005) A 23,000-yr pollen record from Lake Euramoo, Wet Tropics of NE Queensland, Australia. *Quat. Res.* 64, 343 - 35.
- Hutchinson, M.F (1995) Interpolating mean rainfall using thin plate smoothing splines. *International Journal of Geographical Information Systems* 9, 385-403
- Hutley L.B., Doley D., Yates D.J. (1997) Water balance of an Australian subtropical rainforest at altitude: the ecological and physiological significance of intercepted cloud and fog. *Aust J Bot* 45 (2), 311-329
- Kershaw A.P., Bretherton S.C., van der Kaars S. (2007) A complete pollen record of the last 230 ka from Lynch's Crater, north-eastern Australia. *Palaeogeog. Palaeoclim. Palaeoecol.* 251, 23-45.
- Labeyrie L. and Juillet A. (1982) Oxygen isotopic exchangeability of diatom valve silica; interpretation and consequences for paleoclimatic studies. *Geochim. Cosmochim. Acta* 46, 967-975.
- Lachniet M.S. and Patterson W.P. (2002) Stable isotope values of Costa Rican surface waters. *J. Hydrol.* 260, 135-150.
- Lachniet M.S., Patterson W.P. (2009) Oxygen isotope values of precipitation and surface waters in northern Central America (Belize and Guatemala) are dominated by temperature and amount effects. *Earth Planet. Sc. Lett.* 284, 435-446
- Martinelli L.A., Victoria R.L., Sternberg L.S.L., Ribeiro A. and Moreira M.Z. (1996) Using stable isotopes to determine sources of evaporated water to the atmosphere in the Amazon Basin. *J. Hydrol.* 183, 191-204.
- Njitchoua R., Sigha-Nkamdjou L., Dever L., Marlin C., Sighomnou D., and Nia P. (1999) Variations of the stable isotopic composition of rainfall events from the Cameroon rainforest, Central Africa. *J. Hydrol.* 223, 17-23.
- Rieser U., Wust R.A.J. (2010) OSL chronology of Lynch's Crater, the longest terrestrial record in NE-Australia. *Quat. Geochronol.* 5, 233-236
- Salati E., Dall'Ollio A., Gat J. and Matsui E. (1979) Recycling of water in the Amazon basin: an isotope study. *Water Resour. Res.* 15, 1250-1258.
- Savin, S.M., Epstein, S. (1970) The oxygen isotopic compositions of coarse grained sedimentary rocks and minerals. *Geochim. Cosmochim. Acta* 34, 323-329.
- Shahack-Gross R., Shemesh A., Yakir D. and Weiner S. (1996) Oxygen isotopic composition of opaline phytoliths : potential for terrestrial climatic reconstruction. *Geochim. Cosmochim. Acta* 60, 3949-3953.
- Suppiah, R. Collins, D.A. and Della-Marta, P.M. (2001) Observed changes in Australian climate. supporting document for: Climate change projections for Australia. Technical report, CSIRO Atmospheric Research, Aspendale, Australia.

Table 1. Location of the sampled sites and associated climate parameters provided by the ANUCLIM software (D. coast: distance from the coast; Alt: altitude; Max Alt: mean maximum altitude crossed by air masses; MAT: mean annual temperature; MAP: mean annual precipitation; H: relative humidity). Rainforest types from Tracey (1982).  $\delta^{18}\text{O}_{\text{precipitation}}$  values are estimated from (eq.7) and (eq.8) slightly modified after Bowen and Wilkinson (2002).

Sample #	Transect	Lat. S DD	Long. E DD	D. coast m	Alt (m a.s.l.)	Max Alt	MAT Error (°C)	MAP Error (mm)	H (%)	Rainforest type	$\delta^{18}\text{O}_{\text{precipitation}}$ (‰ vs V-SMOW)	Uncertainty
9	Bartle frere	17.28	145.62	70	770	1600	19.8 0.2	1832 275	82	1	-8.97	0.8
38	Bartle frere	17.38	145.79	40	1113	1600	17.9 0.2	4082 612	100	8/9	-7.86	1.0
37	Bartle frere	17.38	145.79	40	1184	1600	17.6 0.2	4411 662	100	8/9	-7.72	1.1
36	Bartle frere	17.38	145.79	40	1222	1600	17.4 0.2	4603 690	100	8/9	-7.64	1.2
35	Bartle frere	17.38	145.80	40	1283	1600	17.0 0.2	4942 741	100	8/9	-7.52	0.0
21	Palmerston	17.57	145.83	30	190	190	22.7 0.2	3333 500	92	24	-3.67	0.0
24	Palmerston	17.61	145.77	30	405	405	21.7 0.2	3154 473	94	1/2	-4.48	0.1
19	Palmerston	17.59	145.62	40	810	810	19.6 0.2	2516 377	92	5a	-5.30	0.2
18	Palmerston	17.53	145.58	40	950	950	19.0 0.2	2281 342	91	5a	-5.58	0.3
17	Palmerston	17.52	145.57	40	1050	1050	18.2 0.2	2583 387	95	24	-5.78	0.3
16	Mt Edith	17.13	145.63	70	670	1500	20.4 0.2	1569 235	72	1	-8.01	0.6
15	Mt Edith	17.11	145.62	70	750	1500	20.0 0.2	1700 255	78	8/9	-8.17	0.6
14	Mt Edith	17.11	145.62	70	840	1500	19.5 0.2	1941 291	82	8/9	-8.35	0.7
11	Mt Edith	17.09	145.62	70	1150	1500	18.0 0.2	3083 462	96	8/9	-8.97	0.8
28	N Cairns	16.47	145.33	30	70	70	24.1 0.2	2040 306	67	1/2	-3.68	0.0
29	N Cairns	16.52	145.39	30	210	210	23.2 0.2	1758 264	65	16g	-4.10	0.1
33	N Cairns	16.81	145.49	30	600	600	22.1 0.2	1500 225	71	1	-4.88	0.2

Table 2. Phytolith assemblages, non phytolith remains and associated measured and calculated isotopic values.

Samples #	Transect	Phytolith types and origin				Non phytolith remains				Isotopic measurements						Isotopic calculations <sup>d</sup>				Corrections				$\Delta^{18}\text{O}_{\text{precip}} - \text{wood phyt.}$ Mean Uncertainty	
		Uncl.	Trees	Palms	Poaceae	Quartz	OM <sup>b</sup>	Fe ox.	Charcoal	$\delta^{18}\text{O}_{\text{measured 1}}$			$\delta^{18}\text{O}_{\text{measured 2}}$			X <sup>c</sup>	$\delta^{18}\text{O}_{\text{silica}}$		$\delta^{18}\text{O}_{\text{silica}}$ <sup>e</sup>		$\delta^{18}\text{O}_{\text{wood phyt.}}$ <sup>f</sup>				
			granulate	Globular	Globular					types <sup>a</sup>	Mean	SD	n	Mean	SD		n	Mean	SD	Mean	SD	Mean	SD		
		(% sum)	(% classified phytoliths)			(% counted particles)				(% vs VSMOW)						(% )		(% vs VSMOW)		(% vs VSMOW)					
9	Bartle Frere	15	48	51	1	1	0	1	0	31.23	0.26	3	35.94	0.11	3	11.1	0.7	35.6	0.1	31.7	1.2	31.9	1.5	40.9	1.5
38	Bartle Frere	4	91	8	1	3	5	0	0	23.50	0.08	2	33.23	0.27	2	23.0	0.7	31.7	0.3	20.8	2.7	21.1	2.7	29.0	2.9
37	Bartle Frere	9	100	0	0	0	12	0	0	27.28	0.39	2	33.38	0.05	2	14.4	0.9	32.6	0.8	26.5	1.5	26.5	1.5	34.2	1.8
36	Bartle Frere	19	99	0	1	0	0	0	0	31.06	0.28	3	34.62	0.13	2	8.4	0.7	34.3	0.1	31.2	0.9	31.2	0.9	38.9	1.4
35	Bartle Frere	13	96	2	2	0	3	0	0	30.23	0.03	2	33.67	0.45	4	2.1	1.1	33.3	0.4	30.2	0.8	30.2	0.8	37.7	1.5
21	Palmerston	39	76	14	10	0	1	0	0	32.43	0.27	3	37.42	0.16	2	11.8	0.7	37.3	0.2	33.3	1.3	33.3	1.3	37.0	1.3
24	Palmerston	10	80	19	1	0	0	0	1	33.53		1	36.69	0.17	2	7.5	1.3	36.6	0.2	34.1	0.8	34.1	0.8	38.6	0.8
19	Palmerston	20	85	6	9	0	1	0	9	31.58	0.68	2	36.17	0.13	2	10.8	1.6	35.9	0.1	32.1	1.2	32.1	1.2	37.4	1.2
18	Palmerston	24	93	5	2	0	0	0	1	32.74		1	36.15	0.08	2	8.1	1.2	36.0	0.1	33.2	0.9	33.2	0.9	38.8	0.9
17	Palmerston	37	83	4	13	1	0	3	1	33.79	0.44	3	37.22	0.36	4	8.1	1.3	37.1	0.4	34.5	0.9	34.8	1.3	40.5	1.3
16	Mt Edith	16	63	34	3	2	0	0	0	30.73	0.29	3	32.97	0.01	2	5.3	0.7	32.7	0.0	30.7	0.5	31.1	1.0	39.1	1.2
15	Mt Edith	11	70	28	2	0	0	0	3	29.80	0.36	2	33.95	0.08	3	9.8	0.9	33.5	0.1	29.7	1.0	29.7	1.0	37.9	1.2
14	Mt Edith	31	77	18	5	1	0	0	0	30.50	0.13	3	35.16	0.05	2	11.0	0.3	34.8	0.5	30.7	1.2	30.9	1.4	39.3	1.6
11	Mt Edith	18	86	8	6	0	0	0	0	28.80	0.12	2	33.85	0.22	2	11.9	0.6	33.3	0.2	28.5	1.3	28.5	1.3	37.5	1.5
28	N Cairns	18	89	9	2	1	0	0	0	32.04	0.39	3	34.79	0.16	2	6.5	1.0	34.5	0.2	32.2	0.7	32.5	1.1	36.1	1.1
29	N Cairns	26	95	0	5	2	0	0	0	33.20	0.50	3	35.25	0.08	2	4.9	1.2	35.1	0.1	33.5	0.5	33.9	1.1	38.0	1.1
33	N Cairns	15	56	42	2	0	2	0	0	30.66	0.24	2	34.89	0.11	2	10.0	0.6	34.5	0.1	30.8	1.1	30.8	1.1	35.7	1.1

(a) Include acicular, elongate echinate, bulliform cells and short cells

(b) Organic matter

(c) Percentage of exchangeable oxygen

(d) Calculated after Crespin et al. (2008) using a Monte Carlo simulation

(e) Corrected for CIE methodological bias (see details in text).

(f) Corrected for the presence of quartz (see details in text).

## Figure Captions

**Figure 1:**  $\delta^{18}\text{O}_{\text{wood phytolith}}$  values vs altitude, mean annual temperature (MAT), mean annual precipitation (MAP) and estimated amount weighted mean annual  $\delta^{18}\text{O}_{\text{precipitation}}$  values. Error bars refer to uncertainties on  $\delta^{18}\text{O}_{\text{precipitation}}$ ,  $\delta^{18}\text{O}_{\text{wood phytolith}}$ , MAP and MAT (Table 1 and 2). Diamonds: points from Bartle Frere; squares: other points. A linear positive correlation appears between  $\delta^{18}\text{O}_{\text{wood phytolith}}$  and  $\delta^{18}\text{O}_{\text{precipitation}}$  values ( $R^2=0.5$ ) when points from Bartle Frere transect (squares) are excluded.

**Figure 2:** Empirical relationship between  $\Delta^{18}\text{O}_{\text{wood phytolith-precipitation}}$  value and mean annual atmospheric temperature (MAT) obtained for the three windward transects. Grey lines: associated uncertainties (Table 1 and 2) and limits of the 95% confidence interval.

**Figure 3:** Correlation between  $1000 \ln \alpha_{\text{vapour-Oexchanged @ CEREGE}} - 1000 \ln \alpha_{\text{vapour-Oexchanged from Labeyrie and Juillet (1982)}}$  and  $\delta^{18}\text{O}_{\text{silica}}$  values obtained at CEREGE before the methodological bias correction.

**Figure 4:** Differences between corrected  $\delta^{18}\text{O}_{\text{silica}}$  and the pooled  $\delta^{18}\text{O}_{\text{silica}}$  values ( $\Delta_{\text{corrected CEREGE-pooled}}$ ) increase with content in total organic carbon (TOC).

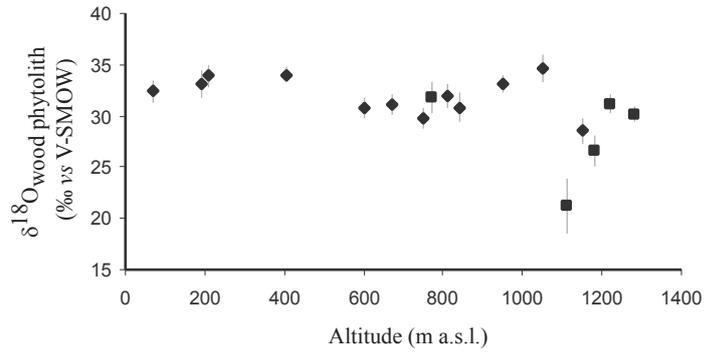
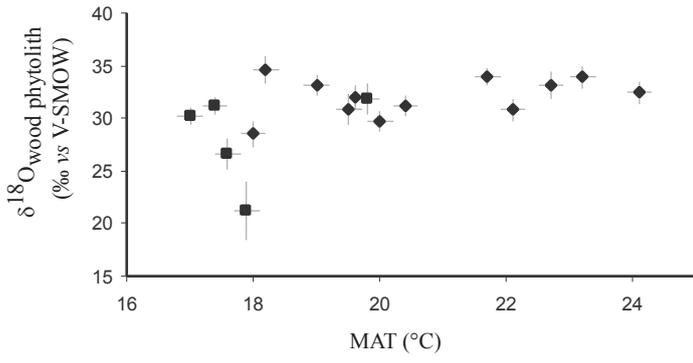
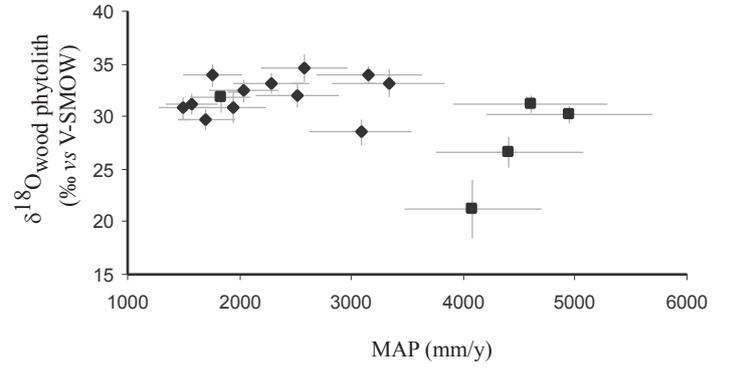
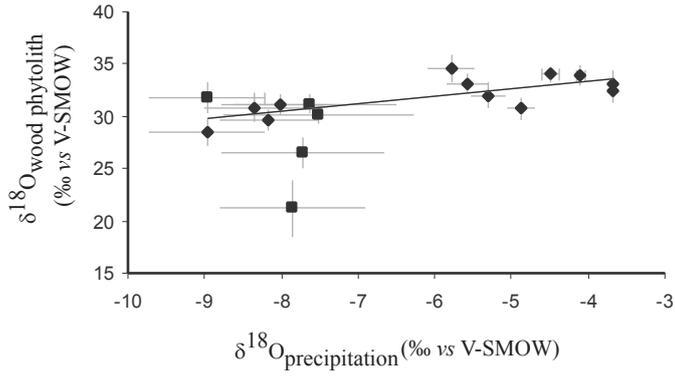


Figure 1

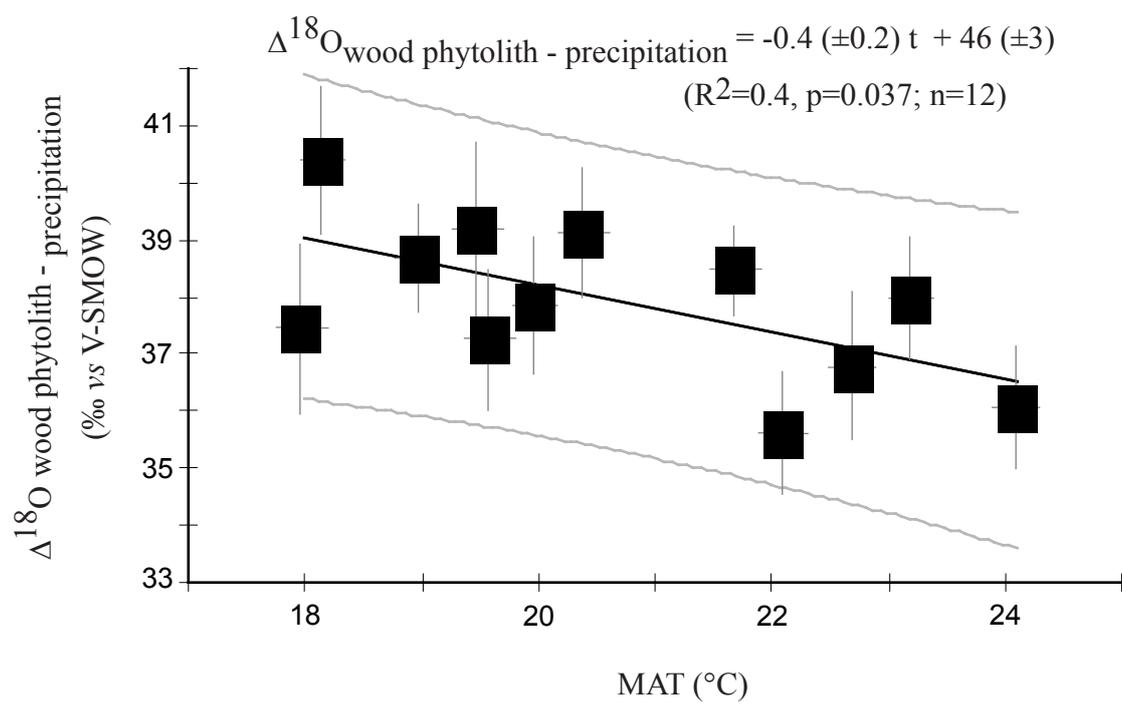


Figure 2

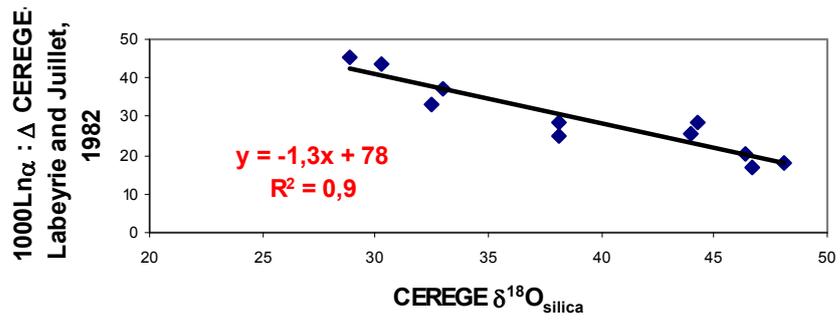


Figure 3

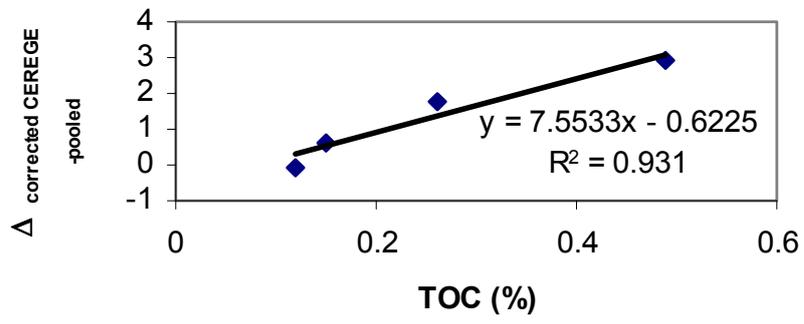


Figure 4