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Title: Temperature responses of the Rubisco maximum carboxylase activity across domains of life: phylogenetic signals, trade-offs and importance for carbon gain

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Abstract

Temperature response of Rubisco catalytic properties directly determines the CO₂ assimilation capacity of photosynthetic organisms as well as their survival in environments with different thermal conditions. Despite unquestionable importance of Rubisco, the comprehensive analysis summarizing temperature responses of Rubisco traits across lineages of carbon-fixing organisms is lacking. Here we present a review of the temperature responses of Rubisco carboxylase specific activity ($k_{\text{cat}}^{\text{c}}$) within and across domains of life. In particular, we consider the variability of temperature responses, and their ecological, physiological and evolutionary controls. We observed over two-fold differences in the energy of activation (ΔH_{a}) among different groups of photosynthetic organisms, and found significant differences between C₃ plants from cool habitats, C₃ plants from warm habitats and C₄ plants. Across all organisms, ΔH_{a} was not related to the species optimum growth temperature (T_{growth}), but was positively correlated with Rubisco specificity factor ($S_{\text{c/o}}$). However, when only land plants were analyzed, ΔH_{a} was positively correlated with both T_{growth} and $S_{\text{c/o}}$, indicating different trends for these traits in plants *vs.* unicellular aquatic organisms, such as algae and bacteria. The optimum temperature (T_{opt}) for $k_{\text{cat}}^{\text{c}}$ correlated with $S_{\text{c/o}}$ for land plants and for all organisms pooled, but the effect of T_{growth} on T_{opt} was driven by species phylogeny. The overall phylogenetic signal was significant for all analyzed parameters, stressing the importance of considering the evolutionary framework and accounting for shared ancestry when deciphering relationships between Rubisco kinetic parameters. We argue that these findings have important implications for improving global photosynthesis models.

Keywords

Activation energy, Adaptation, Carboxylation, Evolution, Photosynthesis, Temperature dependencies

Introduction

The biochemical determinants of photosynthesis belong to the most temperature-responsive physiological processes. Both the carboxylase activity of Rubisco (ribulose-1,5-bisphosphate carboxylase/oxygenase) and the rate of photosynthetic electron transport increase rapidly up to an optimum temperature and sharply decline above the optimum (Berry and Björkman 1980). Inhibition of CO₂ assimilation by temperatures beyond the thermal optimum range affects growth, development and distribution of photosynthetic organisms (Kempner 1963; Hikosaka 1997; Bunce 2000), and has therefore profound ecological and agricultural consequences (Björkman et al. 1980; Ainsworth and Ort 2010). Furthermore, increases in atmospheric CO₂ concentration reduce the effects of CO₂ diffusion conductances on photosynthesis and are thus expected to increase the temperature sensitivity of photosynthesis (Makino 1994; Makino et al. 1994; Cowling and Sage 1998; Hikosaka and Hirose 1998; Sage and Coleman 2001; Sun et al. 2013). This circumstance underscores the importance of improved understanding of variations in temperature responses of biochemical determinants of photosynthesis in models predicting carbon gain under future conditions.

There is a large variation in temperature responses of photosynthesis both within and among species, as well as significant daily and seasonal variations (Björkman et al. 1980; Niinemets et al. 1999; Medlyn et al. 2002a; Medlyn et al. 2002b; Hüve et al. 2006; Kattge and Knorr 2007). Over the short term, such as rapid temperature fluctuations during the day, changes in temperature dependence of photosynthesis may result from alterations in the CO₂ concentration at the carboxylation site and modifications in the rate of ribulose-1,5-bisphosphate (RuBP) carboxylation by Rubisco and RuBP regeneration (Medlyn et al. 2002a; Medlyn et al. 2002b; Kattge and Knorr 2007). Both *in vivo* and *in vitro* approaches have been used to describe the responses of the Rubisco kinetic parameters to the measurement temperature (Badger and Collatz 1977; Monson et al. 1982; Hall and Keys 1983; Jordan and Ogren 1984; Laisk and Oja 1998;

Bernacchi et al. 2001; Walker et al. 2013). The Rubisco carboxylase turnover rate (k_{cat}^c) increases with increasing temperature up to a certain thermal optimum, while the affinity for CO₂ (i.e., the inverse of the Michaelis-Menten constant for CO₂) and the specificity factor ($S_{c/o}$) decrease with increasing temperature (Jordan and Ogren 1984).

Over the longer term, phenotypic changes (acclimation) and evolutionary modifications (adaptation) in photosynthetic responses to temperature are key processes optimizing the carbon balance in the thermal environment the organisms encounter in their habitats (Hikosaka et al. 2006). Hence, species from contrasting climatic environments usually display different photosynthetic temperature dependencies and thermal optima for CO₂ fixation (Berry and Björkman 1980; Larcher 1995; Yamori et al. 2011). Within a single species, abundant data demonstrate acclimation of the temperature dependence of CO₂ fixation to growth temperature (Hikosaka et al. 1999; Yamori et al. 2005). A number of mechanisms have been shown to participate in the acclimation processes, including modifications in the activity and amount of photosynthetic components (Hikosaka et al. 2006; Galmés et al. 2013), expression of a more thermostable Rubisco activase (Salvucci and Crafts-Brandner 2004), and alterations in the thylakoid membrane characteristics that determine the stability of the photosynthetic electron transport chain (Havaux 1998; Sharkey 2005). Recent papers have suggested that Rubisco kinetics can also acclimate to growth temperature (Yamori et al. 2006; Cavanagh and Kubien 2013) and related this adjustment to post-translational modifications and/or differential expression of Rubisco small subunit genes (Yoon et al. 2001).

As regards to the long-term modifications of Rubisco kinetic traits, several lines of evidence suggest that adaptation has occurred to enhance Rubisco catalytic performance in the temperature environment in which the given photosynthetic organism has evolved (Heda and Madigan 1988; Uemura et al. 1997; Zhu et al. 1998; Sage 2002; Galmés et al. 2005). Optimization of Rubisco catalysis to the prevailing temperature is a complex target inevitably bound to the

trade-off between the enzyme's specific activity and its affinity towards CO₂ (Tcherkez et al. 2006; Savir et al. 2010; Galmés et al., 2014a). In hot environments, selection pressure towards Rubiscos with increased specificity towards CO₂ (i.e., higher $S_{c/o}$) has been observed in land plants (Galmés et al. 2005) and in thermophilic red algae (Uemura et al. 1997). The physiological explanation may be that increased $S_{c/o}$ reduces the loss of carbon due to enhanced photorespiration at higher temperatures (Ehleringer and Björkman 1977). On the contrary, at low temperatures, the rate of oxygenation is reduced more than the rate of carboxylation, and therefore selection may have favored increases in k_{cat}^c – even at the expenses of reduced $S_{c/o}$ – to enhance the CO₂ assimilation rate (Cen and Sage 2005). Experimental data suggest that Rubiscos of C₃ plants from cool environments tend to present a higher k_{cat}^c than Rubiscos of C₃ species originating from warm environments (Sage 2002).

Apart from this important trade-off among the Rubisco kinetic traits, the temperature responses of these characteristics can adapt to species temperature environment as well. In species from warm environments, both $S_{c/o}$ (Uemura et al. 1997; Galmés et al. 2005) and k_{cat}^c (Chabot et al. 1972; Weber et al. 1977; Sage 2002) seem to respond more sensitively to increases in temperature compared to species from cool environments. However, relatively few species have been incorporated in drawing the conclusions on the adaptation of Rubisco kinetics to temperature, and a comprehensive analysis is lacking so far. Furthermore, it is important to consider phylogenetic constraints and history of organisms when analyzing the evolution of traits (Ackerly and Reich 1999; Cunningham et al. 1999; Wildner et al. 1999; Draisma et al. 2001). Possible phylogenetic constraints in Rubisco temperature responses would imply that closely related species can have lower trait diversity and can be less adapted to their current growth temperatures due to the past adaptive changes that may constrain the adaptation of their Rubiscos to novel environments. In particular, the evolution of Rubisco amino acid sequence is partly constrained by coevolution of residues and their epistatic interactions (Sen et al. 2011; Wang et al. 2011).

Depending on the composition of amino acid residues they interact with, such co-evolutionary interactions can result in different effects of the same amino acid replacements on Rubisco properties, including temperature responses (Wang et al. 2011; Breen et al. 2012). As a consequence, the convergent evolution of Rubisco enzymes from distant organisms occurring in similar conditions could be achieved via similar or different genetic modifications, e.g. comparative cases of Rubisco adjustments in C₄ plants (Hudson et al. 1990; Christin et al. 2008; Kapralov et al. 2011; Kapralov et al. 2012). In some cases, the adaptive evolution could be even significantly slowed down because of epistasis and differences in the genetic backgrounds (Breen et al. 2012).

The present article compiles the existing literature evidence on temperature responses of Rubisco $k_{\text{cat}}^{\text{c}}$ in a broad range of photosynthetic organisms, including archaea, bacteria, algae and plants, with the following aims: i) to characterize the overall variability in temperature dependencies of $k_{\text{cat}}^{\text{c}}$ across all main lineages of Rubisco possessing taxa; ii) to examine possible trade-offs between $k_{\text{cat}}^{\text{c}}$ adaptation to temperature and Rubisco specificity factor; and iii) to assess phylogenetic signals and constraints in the adaptation of Rubisco temperature dependencies to growth conditions. We test the hypothesis that species occurring in different climates possess Rubiscos with different $k_{\text{cat}}^{\text{c}}$ temperature dependencies; in particular, that species from warmer conditions respond more strongly to temperature over physiological range (greater energy of activation) and have more heat-resistant Rubisco characterized by greater optimum temperatures and energies of deactivation for $k_{\text{cat}}^{\text{c}}$. We argue that from an ecological perspective, a full understanding of photosynthetic adaptation to temperature needs to consider evolutionary changes in the temperature dependence of Rubisco carboxylase activity.

2. Methods

2.1. Data compilation

Data on the *in vitro* Rubisco carboxylase maximum turnover rate (k_{cat}^c , defined as mol CO₂ converted per mol Rubisco active sites per second) at varying temperature were compiled from peer-reviewed literature identified by Thompson-ISI Web of Science (Philadelphia, USA). Only studies reporting measurements for at least three different temperatures during the *in vitro* assay were considered (Table S1). The following information was included in the database: article bibliographic data, species name, the value of k_{cat}^c at different temperatures of measurement and the aqueous-phase CO₂ concentration (C_w) used. Whenever C_w was not reported, it was calculated from the bicarbonate concentration and the acidity constant of dissolved carbon dioxide (pK_a). The value of pK_a was estimated for the given temperature and the solution ionic strength according to Yokota and Kitaoka (1985). Only studies with saturating C_w were included in the final version of the database (Table S1). Across all analyzed studies, the temperature response curves of Rubisco k_{cat}^c were obtained for 49 species (Archaea, $n = 1$; Cyanobacteria, $n = 3$; Proteobacteria, $n = 4$; Rhodophyta, $n = 1$; Chlorophyta, $n = 4$; Spermatophyta, $n = 36$) representing all three domains of life (Archaea, Bacteria, Eukarya).

The average optimum growth temperature (T_{growth}) for each species was obtained from the literature or assigned according to the species climatic range (Table 1). Spermatophytes were further classified according to their photosynthetic mechanism and T_{growth} as warm-temperature C₃ plants ($T_{\text{growth}} \geq 25$ °C; $n = 12$), cool-temperature C₃ plants ($T_{\text{growth}} < 25$ °C; $n = 14$) and C₄ plants ($n = 10$). In this dataset, all multicellular organisms were terrestrial plants, while the rest of the taxa were unicellular aquatic organisms.

2.2. Fitting the temperature responses

The units for k_{cat}^c varied among studies, and due to lack of relevant information, unit interconversion was sometimes problematic or even impossible. Examples of problematic units included radioactive assays reporting RubP carboxylation rate in counts per time, studies

expressing k_{cat}^c per leaf mass or crude protein and studies where the degree of Rubisco purification was not reported. Therefore, to directly compare the shapes of the temperature responses, we normalized all k_{cat}^c values with respect to 25 °C. Whenever a given study did not include measurements at 25 °C, we first fitted the temperature response in the original units as described below (Eqs. 1 and 2) and calculated the predicted k_{cat}^c value at 25 °C. This reference value was further used in data normalization.

Truncated temperature response curves with data covering only the part below the optimum temperature were available for 26 species, while full temperature responses with data extending above the optimum temperature were available for 23 species. For both truncated and full temperature responses, we fitted the initial exponential part of the temperature dependence of k_{cat}^c by the Arrhenius-type equation (Badger and Collatz 1977; Harley and Tenhunen 1991) that assumes that the activity continues to increase exponentially with increasing temperature:

$$k_{\text{cat}}^c = e^{c - \Delta H_a / RT} \quad (1)$$

where c is the scaling constant, ΔH_a (kJ mol⁻¹) is the activation energy, T (K) is the temperature and R (kJ mol⁻¹ K⁻¹) is the gas constant. For species with full temperature responses, k_{cat}^c was fitted with an equation including both the entropy of deactivation (ΔS , kJ mol⁻¹ K⁻¹) and the deactivation energy (ΔH_d , kJ mol⁻¹) terms (Harley and Tenhunen 1991):

$$k_{\text{cat}}^c = \frac{e^{c - \Delta H_a / RT}}{1 + e^{(\Delta S T - \Delta H_d) / RT}} \quad (2)$$

The two additional characteristics, ΔS and ΔH_d characterize the reversible (or irreversible at excessive temperatures) denaturation of proteins and jointly determine the denaturation rate constant (Johnson et al. 1942; Gummadi 2003).

Both Eq. 1 and Eq. 2 were fitted to the data by iteratively minimizing the sum of squares between the measured and predicted values of k_{cat}^c using the Microsoft Excel Solver function (Microsoft, Redmond, WAC, USA). For Eq. 1 and 2, the fraction of variance explained (r^2) was

defined as the square of the correlation coefficient observed for linear regressions between predicted vs. measured values. From Eq. 2, the optimum temperature (T_{opt}) for k_{cat}^c was calculated (Niinemets et al. 1999):

$$T_{\text{opt}} = \frac{\Delta H_d}{\Delta S + R \ln \left(\frac{\Delta H_d}{\Delta H_a} - 1 \right)} \quad (3)$$

The activation energies determined by Eqs. 1 and 2 were numerically similar and strongly correlated ($y = 1.003x$, $r^2 = 0.93$). Thus, for species with full temperature responses, ΔH_a was taken from Eq. 2, and for the remaining species, ΔH_a corresponds to Eq. 1. As Eq. 1 predicts, the initial response of k_{cat}^c to increasing temperature is exponential (Fig. 1S). Thus, we also calculated the slopes of the linear regressions among $\ln k_{\text{cat}}^c$ vs. T to facilitate the comparison of the thermal sensitivity of the carboxylase reaction of Rubisco from distant phylogenetic groups (Fig. 1). In addition, we calculated the ratio of k_{cat}^c at 5 °C to that at 25 °C to assess the performance of Rubisco at low temperatures. This ratio was calculated using Eqs. 1 or 2 and only when low temperature measurements (10 °C or less) were available.

Conventional analysis (i.e., not corrected by the phylogenetic signal) consisted of one-way ANOVA and correlation for linear regressions. For all the parameters studied, an univariate model of fixed effects was assumed. The univariate general linear model for unbalanced data (Proc. GLM) was applied and significant differences among groups of species were revealed by Duncan tests using IBM SPSS Statistics 20 software package (SPSS Inc., Chicago, IL, USA). The relationships among the parameters of the temperature response curve of k_{cat}^c and Rubisco specificity factor ($S_{c/o}$) were tested with the square of the correlation coefficient observed for linear regressions using the tool implemented in SigmaPlot 11.0 (Sigma, St Louis, MO, USA). All statistical tests were considered significant at $P < 0.05$.

2.3. Tests for phylogenetic signals and trait correlations using phylogenetically independent contrasts

Provided species sampling is random and adequate, correlations observed within such a dataset will reflect the basic correlative variation patterns operative in nature (Westoby et al. 1998; Westoby et al. 2002). However, non-adequate sample size and non-random sampling could strongly bias the conventional analysis. In particular, correlations arising within groups of closely related taxa might be driven by a phylogenetic signal rather than reflect adaptive relationships, thereby reducing the generality of observed correlations. In fact, closely related taxa are not necessarily independent data points and, therefore, are sometimes considered to violate the assumption of randomized sampling employed by conventional statistical methods (Felsenstein 1985). To overcome this issue, we assembled a composite phylogeny of all analyzed species using available 16S ribosomal RNA and *rbcL* sequences from GenBank (<http://www.ncbi.nlm.nih.gov>) as well as the *rbcL*-based phylogeny of Spermatophyta using a maximum-likelihood inference conducted with RAxML version 7.2.6 (Stamatakis 2006). *RbcL* sequences of congeneric taxa were used for a few species with no available *rbcL* sequences (e.g., the *rbcL* of *Alopecurus pratensis* was used as substitute for the missing *rbcL* of *A. alpinus*). These phylogenies (Fig. S2), as well as their pruned versions containing only aquatic unicellular organisms and only C₃ plants were further used to test for phylogenetic signals and trait correlations with independent contrasts using the AOT module of PHYLOCOM (Webb et al. 2008). The phylogenetic signal characterizes the tendency for close relatives to resemble each other (Blomberg and Garland 2002), while the independent contrast analysis uses the phylogenetic information to convert the interspecific data into identically distributed and independent values that can be used in conventional statistical analyses without interfering phylogenetic signal (Garland et al. 1999). Correlations of phylogenetically independent contrasts (PicR) were run among the parameters analyzed and considered significant at $P < 0.05$.

3. Results

3.1 Temperature responses of k_{cat}^c : general patterns

The fraction of variance explained (r^2) by equations 1 and 2 was always >0.97 (on average 0.98), indicating that both equations provided excellent fits to the data. The energies of activation of k_{cat}^c (ΔH_a) varied across species between 24.4 kJ mol⁻¹ (green alga *Chlamydomonas reinhardtii*) and 86.1 kJ mol⁻¹ (C₃ herbaceous perennial plant *Trifolium repens*; Table 1). Across all organisms, ΔH_a was not related to species optimum growth temperature (T_{growth}). In fact, the values observed for the thermotolerant species *Cyanidium caldarium* and *Thermococcus kodakariensis* were among the highest and lowest, respectively, within the database (Table 1). When the phylogenetic groups were compared, the green algae – Chlorophyta – possessed the lowest ΔH_a of 26.7 kJ mol⁻¹, while the red algae – Rhodophyta (i.e., *Cyanidium caldarium*) – had the highest ΔH_a of 76.3 kJ mol⁻¹ (Table 2).

Linearization of the initial exponential response by a natural logarithmic transformation was used for the alternative comparison of thermal sensitivity of the Rubisco carboxylase reaction between distant phylogenetic groups (Fig. 1A). Rhodophyta and Streptophyta were the groups with the highest slope of $\ln k_{cat}^c$ vs. temperature, while Chlorophyta had the lowest slope. Within plants (Spermatophyta), the slope of the relationship $\ln k_{cat}^c$ vs. temperature was higher for C₃ plants from warm habitats compared to C₃ plants from cool habitats and C₄ plants (Fig. 1B). This trend was corroborated by the higher ΔH_a of the C₃ species from warm habitats (Table 2).

3.2 Optimum temperature for k_{cat}^c

Values of k_{cat}^c were available at temperatures above the optimum for 23 species, allowing for calculation of parameters describing both the activation and deactivation phases of the temperature response. Different patterns were evident among the phylogenetic groups (Fig. 2A). The

extremophile archaeon *Thermococcus kodakariensis* showed exceptionally high optimum temperature (T_{opt}) of 90.7 °C (Table 1), although we note that temperature responses of non-thermophilic archaea were not available. Among the remaining groups, Cyanobacteria was the second after Archaea, with T_{opt} of 59.6 °C. The land plants presented a lower T_{opt} (52.7 °C), but still higher than Proteobacteria, Chlorophyta and Rhodophyta (Table 2 and Fig. 2A). Two proteobacterial species, *Chromatium vinosum* and the endosymbiont of the mollusk *Alviniconcha hessleri*, possessed the lowest T_{opt} of only about 37 °C (Table 1).

Among the land plants, the grass *Alopecurus alpinus* had the lowest T_{opt} of 48.8 °C, and the herbaceous perennial *Astragalus rafaensis* showed the highest value of 58.7 °C. These two plant species could be representative of two climatic extremes. *Alopecurus alpinus* inhabits mountain and boreal regions, while *A. rafaensis* occurs in dry desert areas. In fact, C_3 plants from warm habitats had significantly higher T_{opt} values than those in C_3 plants from cool habitats and those in C_4 species (Table 2 and Fig. 2B).

3.3. Correlations among the temperature response curve parameters

The results of conventional statistical analyses and those corrected for the phylogenetic signal were in most cases qualitatively identical. Thus, we first report the results of the phylogenetically-corrected analyses and then highlight the key differences in conventional analyses.

When all species were analyzed together, the phylogenetic signal was significant for all analyzed parameters (c , ΔH_a , ΔH_d , ΔS , T_{opt} , $S_{c/o}$) at $P < 0.05$, except for T_{growth} ($P = 0.06$). A number of relationships among the parameters characterizing the temperature response of k_{cat}^c were significant (Table 3). Both the correlation between ΔH_a and the scaling constant c , and the correlation between the values for ΔH_d and the entropy term (ΔS) were positive and highly significant according to correlations of phylogenetically independent contrasts (PicR; Table 3) and conventional statistics (Fig. 3). ΔH_a was inversely related to the performance of Rubisco

carboxylase reaction at low temperatures (taken as the ratio of activities at 5°C/25°C; $r = -0.693$, $P < 0.05$). The specificity factor of Rubisco ($S_{c/o}$) was positively related to ΔH_a according to PicR (Table 3) and the conventional analysis (Fig. 4), suggesting that the evolution towards higher affinity to CO₂ and enhanced temperature responsiveness might have occurred simultaneously.

Three pairs of parameters (c vs. ΔH_a ; ΔH_d vs. ΔS ; ΔH_d vs. T_{opt}) exhibited significant positive correlations both when all species were analyzed together as well as in each of the three subsets analyzed separately (unicellular aquatic organisms, land plants, C₃ plants), indicating common trends across all Rubiscos. However, other parameters correlated across some subsets of organisms, but not in others, suggesting different trends for these parameters in plants vs. unicellular organisms. For example, $S_{c/o}$ was positively correlated with all studied parameters in plants, but only with half of them in unicellular aquatic organisms (Table 3). Differently from the phylogenetically independent contrast analyses, T_{opt} and ΔH_a were positively correlated within Spermatophyta ($r^2 = 0.76$, $P < 0.01$; Fig. 5).

3.4. Effects of growth environment on the temperature response curve parameters

According to PicR, $S_{c/o}$ vs. T_{growth} exhibited significant positive correlations for all species analyzed together as well as for each of the three subsets analyzed separately (Table 3). No significant relationship between ΔH_a and T_{growth} was observed when all taxa were included in the independent contrast correlation analysis, but there was a significant positive correlation for plants (Table 3). In contrast, ΔH_d and T_{growth} were positively correlated for all data pooled, but not for individual groups, except for C₃ plants (Table 3).

The optimum temperature for k_{cat} (T_{opt}) was not correlated with T_{growth} according to PicR either for all data pooled or for any of the groups (Table 3). In contrast, according to the conventional analysis, T_{opt} and T_{growth} were significantly correlated for all data pooled ($r^2 = 0.48$, P

< 0.001). This discrepancy reflects the coincidence of high T_{opt} and T_{growth} in some phylogenetic groups (Archaea and Cyanobacteria, Table 2) but not in others.

3.5. Contrasting temperature responses of k_{cat}^c : importance for photosynthesis modeling

The photosynthesis model of Farquhar et al. (1980) was used to quantify the effect, in terms of leaf photosynthetic carbon assimilation, of the observed contrasting temperature responses of k_{cat}^c of Rubisco between C₃-cool and C₃-warm species. Assuming the same k_{cat}^c value at 25°C (2.5 s⁻¹) and concentration of active Rubisco (2 g m⁻²) for both C₃-cool and C₃-warm species, important differences were observed between the two groups. The optimum temperature for maximum Rubisco CO₂ assimilation potential (A_{Rubisco}) increased with increasing C_c (Fig. 6). At temperatures above 25 °C, a greater thermal tolerance of k_{cat}^c of Rubisco from C₃-warm species resulted in higher A_{Rubisco} as compared to the Rubisco of C₃-cool species at a C_c of 400 μmol mol⁻¹, corresponding to future moderately elevated ambient CO₂ concentrations of 600-800 μmol mol⁻¹ (Fig. 6A-C).

To interpret these results in terms of leaf net CO₂ assimilation rate (A_N), it is important to consider that A_N temperature response depends on the temperature effects on A_{Rubisco} , mitochondrial respiration rate and Rubisco activase. Making the simplifying assumption that both C₃-cool and C₃-warm species have the same temperature responses for the mitochondrial respiration and Rubisco activase, the impact of the different thermal sensitivities of k_{cat}^c of Rubisco on A_N was lowered, but was still considerable. For instance, at 33 °C, A_N of C₃-warm species was 19% higher than that of C₃-cool species under a C_c of 120 μmol mol⁻¹, and the corresponding difference was 12% at a C_c of 400 μmol mol⁻¹. Moreover, when considering different thermal sensitivities of both the Rubisco activase (Salvucci and Crafts-Brandner 2004) and the Rubisco k_{cat}^c between the two groups, the simulation predicts at 33 °C 200% higher A_N for C₃-warm species

than for C₃-cool species under a C_c of 120 μmol mol⁻¹, and 143% higher A_N under a C_c of 400 μmol mol⁻¹ (Fig. 6D-F).

4. Discussion

4.1. The temperature dependence parameters of k_{cat}^c from different phylogenetic and climatic groups and correlations among them

The differences among the phylogenetic groups in the initial slope of the $\ln k_{\text{cat}}^c$ vs. temperature response (Fig. 1A) are indicative of the presence of adaptive trends in the thermal response of Rubisco carboxylase from distant photosynthetic organisms. Among these trends, changes in the activation energy (ΔH_a) may be an important environmental adaptation on an evolutionary time-scale (Somero 1969). The activation energies of k_{cat}^c calculated in the present survey, although higher than the Arrhenius activation energies reported by Tcherkez et al. (2006), confirmed the tendency of higher values of ΔH_a for Rhodophyta and Spermatophyta as compared to other groups (Table 2). In addition, red algae and plant species presented the highest values for both the ΔH_a and $S_{c/o}$, and there was a positive correlation among these two Rubisco traits (Table 3 and Fig. 4). This relationship has been previously interpreted as the expected consequence of the evolutionary optimization of the transition state structure for the Rubisco carboxylation reaction (Tcherkez et al. 2006). However, this correlation is relatively scattered, suggesting that there is room for adaptation in ΔH_a at any given value of $S_{c/o}$, implying that different “optimal” Rubiscos can exist in different conditions.

It has been hypothesized that the prevailing thermal range of each species niche is the main environmental factor driving the evolution of Rubisco response to temperature (Sage et al. 2002; Tcherkez et al. 2006). However, this hypothesis could only be partially confirmed by the data from the present survey, as the correlation between ΔH_a and the optimum growth temperature (T_{growth}) was significant only within land plants (Table 3). This might be due to the limited coverage of the

thermal response of Rubisco from other groups. In particular, both the Archaea and Rhodophyta groups were represented by a single thermophilic species each, while non-thermophilic species are also known within these groups (Kvist et al. 2005). Therefore, further analysis of the thermal response of Rubisco carboxylation in a number of species from these uncovered groups is pivotal for obtaining the unbiased perspective of the evolution of $k_{\text{cat}}^{\text{c}}$ response to temperature.

Provided that the temperature of species environment drives the evolution of the thermal sensitivity of Rubisco, it could be argued that Rubiscos from aquatic organisms might present less plasticity to temperature change in comparison to terrestrial Rubiscos, subject to higher thermal fluctuations (Chabot et al. 1972). Certainly, terrestrial Spermatophyta species tended to show higher values for ΔH_{a} of $k_{\text{cat}}^{\text{c}}$ than the aquatic groups (Table 2). However, the highest values for some of these parameters were observed among aquatic species (Table 1). Again, increasing available data for Rubiscos from aquatic environments (including aquatic Spermatophyta) is required to complete the picture of the thermal response of Rubisco carboxylation.

Initial explorations on the evolutionary divergence in the energy of activation of $k_{\text{cat}}^{\text{c}}$ reported lower activation energies in plants adapted to low temperatures (Phillips and McWilliam 1971). Later, Sage (2002) suggested a trend for increased activation energy of $k_{\text{cat}}^{\text{c}}$ in C_3 plants from cool habitats and C_4 plants compared to C_3 plants from warm habitats, but differences between these groups were not significant. The number of land plant species included in the present study was increased over two-fold compared to the study by Sage (2002), while the species distribution among the groups was more uniform. Thus, in our database, differences in ΔH_{a} between C_3 plants from cool habitats, C_4 plants and C_3 plants from warm habitats became statistically significant (Table 2). The observed differences confirmed the hypothesis that Rubisco of C_3 species from warm environments has evolved towards a more plastic response to temperature changes. This finding is in agreement with the idea that in environments of limited thermal energy, natural selection might favor enzymes which are capable of lowering the energy of

activation to minimal levels (Chabot et al. 1972). Although the differences in $S_{c/o}$ among land plant groups were not significant in our study (Table 2), selection pressure for higher $S_{c/o}$ in C_3 plants from warm environments has been documented (Galmés et al. 2005). In addition, a lower $S_{c/o}$ in C_4 plants has also been reported (e.g., Kubien et al. 2008). There is also evidence that in cool environments, the selection pressure favors Rubiscos with higher k_{cat}^c (Sage 2002; Yamori et al. 2009), and hence lower $S_{c/o}$, given the tradeoff between k_{cat}^c and $S_{c/o}$ (Badger and Andrews 1987; Tcherkez et al. 2006; Savir et al. 2010). According to the transition state theory for the Rubisco carboxylation reaction (Tcherkez et al. 2006), $S_{c/o}$ correlates positively with ΔH_a (Table 3 and Fig. 4). This fact suggests that evolution towards increased specificity for CO_2 in warm environments was achieved together with a higher sensitivity of Rubisco kinetics to variation in temperature. Alternatively, it may simply reflect Rubisco adaptation to both hotter and more fluctuating thermal environments, which might have been somewhat constrained by the trade-off between CO_2 affinity and thermal response. The pertinent question to test in the future, when more data for temperature responses in distinct phylogenetic groups becomes available, is how fast the adaptation of Rubisco temperature responses can occur, and whether there is higher variability in Rubisco temperature responses in phylogenetic lineages which have experienced wider range of temperatures during their evolution.

4.2. Variation in the optimum temperature for k_{cat}^c

Rubisco has been classified as a protein resistant to high temperature with k_{cat}^c increasing up to approximately 50 °C (Tieszen and Sigurdson 1973; Salvucci et al. 2001). The present study confirms this observation, but also reveals the existence of an important variation in the optimum temperature for k_{cat}^c (T_{opt}) among phylogenetic groups (Table 2 and Fig. 2). It is therefore pertinent to ask how different values of T_{opt} are achieved in different organisms by alterations in temperature response curve parameters, ΔH_a , ΔH_d and ΔS . Although T_{opt} as the outcome of activation and

deactivation processes is functionally related to all these parameters (Eq. 3), a given value of T_{opt} was obtained by different combinations of these traits in different organisms (Table 2), and the parameters correlations differed among the groups and were partly driven by species phylogeny (Table 3). This fact implies that temperature response curves sharing the same T_{opt} had different shapes across photosynthetic organisms. In most cases, T_{opt} was driven by changes in the deactivation, as demonstrated by significant correlations of T_{opt} with ΔH_d and ΔS (Table 3).

In plants, the conventional statistical analysis further highlighted a positive correlation of T_{opt} with ΔH_a (Fig. 5) and a negative correlation with Rubisco carboxylase performance at low temperatures, approximated by the ratio of carboxylation rates at 5 °C/25 °C ($r^2 = 0.64$, $P < 0.01$). These correlations seem to confirm the existence of a trade-off between Rubisco thermal stability and its performance at low temperatures postulated by previous studies (Ford 1979; Devos et al. 1998). However, these relationships were not significant when the phylogenetic signal was accounted for (Table 3). This discrepancy among two analyses suggests that the evolutionary history may have shaped the k_{cat}^c temperature response, i.e., different lineages have differently changed T_{opt} and the activation energy through the evolution.

4.3. Is the variation in the optimum temperature for k_{cat}^c physiologically significant?

Although Rubisco is among the key players controlling the temperature dependence of photosynthetic biochemistry (Sharkey 2005; Hikosaka et al. 2006; Yamori et al. 2006; Sage and Kubien 2007), T_{opt} of k_{cat}^c does not match with T_{opt} of the photosynthetic CO_2 assimilation (Yamori et al. 2014). In general, T_{opt} of k_{cat}^c is higher than the optimum for photosynthetic CO_2 fixation. The discrepancy between the temperature optima of k_{cat}^c and photosynthesis is partially due to the decreased affinity of Rubisco for CO_2 (i.e. higher K_c) and lower $S_{c/o}$ (Jordan and Ogren 1984; Brooks and Farquhar 1985), and the decreased CO_2/O_2 concentration ratio in solution (Ku and Edwards 1977) at higher temperatures. In addition, the activation energy of the Rubisco oxygenase

reaction has been documented to be similar to that of $k_{\text{cat}}^{\text{c}}$ (Badger and Collatz 1977). Furthermore, Rubisco carboxylation capacity at high temperatures can also be limited by enhanced production of side-products from RuBP during catalysis and Rubisco deactivation through decreased Rubisco activase activity at higher temperatures (Sharkey et al. 2001; Salvucci and Crafts-Brandner 2004; Kim and Portis 2006; Yamori and von Caemmerer 2009).

Although the heat resistance of Rubisco alters only moderately the optimum thermal range for CO_2 assimilation under current ambient CO_2 concentrations, there may be other benefits of improving the heat resistance of Rubisco in hotter environments. Given that Rubisco is the most abundant protein in leaves, thermal damage of Rubisco would obviously constitute a very high cost for the plant. Severe damage of leaf photosynthetic machinery typically occurs at relatively high temperatures, above 46-50 °C (Seemann et al. 1984; Bilger et al. 1987; Hüve et al. 2011; Sun et al. 2013). Such a high temperature threshold could not be achievable without maintenance of the integrity of enzymatic machinery. Surprisingly, heat-resistant Rubisco, close or beyond 50 °C was also observed in C_3 -cool climate species (Table 1). However, even in cool climates, leaves may be exposed to high temperatures, close to 50 °C during sunflecks of moderate duration (Hamerlynck and Knapp 1994; Singsaas et al. 1999; Singsaas and Sharkey 2000; Valladares and Niinemets 2007), implying that even in relatively cool environments, high Rubisco thermal resistance could be adaptive.

4.4. Implications for modeling photosynthesis

The maximum velocity of Rubisco carboxylation (V_{cmax}) used in photosynthesis models is given as the Rubisco specific carboxylase activity ($k_{\text{cat}}^{\text{c}}$) times the number of Rubisco active sites per leaf area (Rogers 2014). Thus, in all process-based photosynthesis models simulating carbon gain in the field, temperature response of Rubisco kinetics, like $k_{\text{cat}}^{\text{c}}$, is an integral component driving the accuracy of the predicted temperature responses of photosynthesis (e.g. Farquhar et al. 1980;

Harley and Tenhunen 1991). In general, photosynthesis models are applied assuming that the temperature responses of k_{cat}^c (or V_{cmax}) are invariable across species (Niinemets and Tenhunen 1997; Bernacchi et al. 2001; Sharkey et al. 2007; Díaz-Espejo, 2013; Rogers 2014). Actually, many contemporary studies, irrespective of the species considered, use the temperature functions provided for tobacco (Bernacchi et al. 2001, 2003) to model photosynthesis in a range of environmental conditions (e.g., Yamori and von Caemmerer 2009; Galmés et al. 2011; Bermúdez et al. 2012), while many others use spinach (Jordan and Ogren 1984) Rubisco kinetics (e.g., Harley et al. 1992; Niinemets et al. 2009; Sun et al. 2012). However, some evidence already exists suggesting that the temperature response of V_{cmax} might vary among species (Zhu et al. 1998; Hikosaka et al. 2006; Archontoulis et al. 2012; Walker et al. 2013).

Modelling the effect of the different thermal sensitivity of k_{cat}^c of Rubisco from C₃-cool and C₃-warm plant species on the Rubisco CO₂ assimilation potential (A_{Rubisco}) demonstrated the improved performance of Rubisco from C₃-warm at high temperatures. As expected (Sage 2002), the benefit of a C₃-warm Rubisco at elevated temperatures increased with the concentration of CO₂ at the site of carboxylation (Fig. 6A-C). These results support recent claims that the assumption of a “constant” Rubisco can lead to a major bias in photosynthesis simulations (Díaz-Espejo 2013; Walker et al. 2013; Galmés et al. 2014a).

The effect of the contrasting temperature response of Rubisco k_{cat}^c between C₃-cool and C₃-warm on the CO₂ assimilation rate (A_N) increased after accounting for the existence of different thermal adaptation of Rubisco activase (Fig. 6 D-F). This fact indicates that photosynthetic acclimation to moderately high temperatures necessitates the concomitant optimization of the thermal response of both Rubisco kinetics and Rubisco activase.

4.5. Conclusions and a prospectus for future work

Inhibition of photosynthesis by heat stress is one of the main concerns for agriculture in the XXI century when significant proportion of arable lands would be facing not only increased mean temperatures, but also the increased frequency and duration of heat waves. Further exploration of the variation in the response to temperature of the Rubisco catalytic parameters may allow the discovery of Rubisco versions resistant to high temperatures, in particular in groups underrepresented in the current analyses, such as Archaea and Rhodophyta. Better coverage of the global Rubisco spectrum would be also essential for the development of next generation global photosynthesis models that should consider interspecific variation in k_{cat}^c within and across domains of life.

One of the next steps should be uncovering genetic and structural basis of differences in the temperature sensitivity of Rubiscos from contrasting environments and implementing these findings to customize crop enzymes. Recent advances in our knowledge on Rubisco structure and its folding and assembly (Liu et al. 2010; Bracher et al. 2011; Whitney et al. 2011a) coupled with tools for Rubisco manipulation *in planta* (Whitney and Sharwood 2008) and the first successful cases of engineering plant Rubiscos with changed kinetics (Sharwood et al. 2008; Ishikawa et al. 2011; Whitney et al. 2011b) are promising for future Rubisco alteration in crops including improved thermotolerance. While some Rubisco engineering attempts are trying to create a super-enzyme that overcomes the limitations of natural evolution, an alternative strategy could be data-mining of existing Rubisco diversity in nature and modifying crop enzymes with genetic and structural solutions originated during the Rubisco evolution. The later strategy is supported by modeling studies predicting that even moderate improvements in the crop Rubisco performance could result in significant yield increases (Zhu et al. 2004; von Caemmerer and Evans 2010; Zhu et al. 2010). New methods of DNA and amino acid sequence analyses within a phylogenetic framework allow pinpointing amino acid replacements within Rubisco which are responsible for alteration of its kinetics (Kapralov and Filatov 2007; Christin et al. 2008; Kapralov et al. 2011;

Kapralov et al. 2012; Galmés et al. 2014b,c). Similar approaches could be applied to find the key sites responsible for temperature sensitivity and guide the Rubisco engineering attempts. Customized crop Rubiscos fine-tuned to the local climates and coupled with more thermotolerant versions of Rubisco activase (Kurek et al. 2007) would be required for the next green revolution based on engineering of the photosynthetic CO₂ fixation to increase crop productivity in warmer climates to come (Ainsworth et al. 2012; Evans 2013; Parry et al. 2013).

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Figure captions

Fig. 1 Values of the natural logarithm of Rubisco maximum carboxylase turnover rate normalized to 25°C ($\ln k_{\text{cat}}^{\circ}$) at a range of temperatures in (A) all phylogenetic groups, and (B) in land plants only. Values for $\ln k_{\text{cat}}^{\circ}$ were obtained at discrete temperatures after applying equation 1 (see Methods); means and standard errors are presented. Symbols for the phylogenetic groups in (A): empty downward triangles and dotted line, Archaea ($n = 1$); empty upward triangles and short-dashed line, Proteobacteria ($n = 4$); empty circles and dash-dotted line, Cyanobacteria ($n = 3$); empty squares and dash-dotted-dotted line, Chlorophyta – green algae ($n = 4$); diamond and long-dashed line, Rhodophyta – red algae ($n = 1$); filled squares and solid line, Spermatophyta – plants ($n = 36$). Symbols for Spermatophyta groups in (B): solid downward triangles and dotted line, C_3 plants from cool habitats ($n = 12$); solid upward triangles and long-dashed line, C_3 plants from warm habitats ($n = 14$); solid circles and line, C_4 plants ($n = 10$). The cool-temperature C_3 species were defined as those with the optimum growth temperature (T_{growth}) of less than 25 °C, while the warm-temperature species as those with $T_{\text{growth}} \geq 25$ °C.

Fig. 2 Values of the maximum carboxylase turnover rate (k_{cat}°) of Rubisco normalized to 25°C at a range of temperatures in (A) all phylogenetic groups, and (B) in land plants only. Values for k_{cat}° were obtained at discrete temperatures and at the optimum temperature after applying equations 2 and 3 (see Methods); means and standard errors are presented. Symbols for the phylogenetic groups in (A): empty downward triangle, Archaea ($n = 1$); empty upward triangles, Proteobacteria ($n = 4$); empty circles, Cyanobacteria ($n = 2$); empty squares, Chlorophyta – green algae ($n = 4$); diamond, Rhodophyta – red algae ($n = 1$); filled squares, Spermatophyta – land plants ($n = 11$). Symbols for the land plants groups in (B): solid downward triangles and dotted line, C_3 plants from cool habitats ($n = 4$); solid upward triangle and long-dashed line, C_3 plants from warm habitats ($n = 5$); solid circles and solid line, C_4 plants ($n = 2$). The inset graph in (A) shows the

values of k_{cat}^c of Rubisco for Archaea. The inset graph in (B) represents land plant k_{cat}^c values normalized to the optimum temperature.

Fig. 3 The relationship between: (A) activation energy (ΔH_a) and scaling constant (c); (B) ΔH_a and energy of deactivation (ΔH_d); and (C) ΔH_d and entropy term (ΔS), for all phylogenetic groups. Means and standard errors are presented. r^2 and P are based on non-phylogenetically controlled data. Symbols for the phylogenetic groups: empty downward triangles, Archaea ($n = 1$); empty upward triangles, Proteobacteria ($n = 4$); empty circles, Cyanobacteria ($n = 3$); empty squares, Chlorophyta – green algae ($n = 4$); diamond, Rhodophyta – red algae ($n = 1$); filled squares, Spermatophyta – seed plants ($n = 36$).

Fig. 4 The relationship between activation energy (ΔH_a) and Rubisco specificity factor ($S_{c/o}$) for all phylogenetic groups. r^2 and P are based on non-phylogenetically controlled data. Symbols for the phylogenetic groups: empty upward triangles, Proteobacteria ($n = 1$); empty circles, Cyanobacteria ($n = 3$); empty squares, Chlorophyta – green algae ($n = 2$); diamond, Rhodophyta – red algae ($n = 1$); filled squares, Streptophyta – land plants ($n = 14$). Means and standard errors are presented

Fig. 5 The relationship between activation energy (ΔH_a) and optimum temperature (T_{opt}) for land plants. r^2 and P are based on non-phylogenetically controlled data. Symbols for the groups: solid downward triangles, C_3 plants from cool habitats ($n = 4$); solid upward triangles, C_3 plants from warm habitats ($n = 5$); solid circles, C_4 plants ($n = 2$)

Fig. 6 Modeling the effect of the different thermal sensitivity of k_{cat}^c of Rubisco from C_3 -cool (filled circles) and C_3 -warm (empty circles) plant species on (A, B, C) the Rubisco CO_2 assimilation potential (A_{Rubisco}) and (D, E, F) the leaf net CO_2 assimilation rate (A_N) at chloroplastic

CO₂ concentrations (C_c) of (A, D) 120, (B, E) 200 and (C, F) 400 $\mu\text{mol mol}^{-1}$. The optimum temperature giving maximum values of A_{Rubisco} and A_N is indicated for each plot. To model A_{Rubisco} at different temperatures, the values for the temperature dependence parameters of k_{cat}^c for C₃-cool and C₃-warm were taken from Table 2, assuming a k_{cat}^c value of 2.5 s⁻¹ at 25°C for both C₃-cool and C₃-warm. The Rubisco Michaelis-Menten constant for CO₂ (K_c) and O₂ (K_o) and the specificity factor ($S_{c/o}$), as well as their temperature dependence, were assumed to be those reported for *Spinacea oleracea* (Jordan and Ogren 1984) in both C₃-cool and C₃-warm modeling. Rubisco concentration was assumed to be invariable at 2 g m⁻². As for A_N , changes in the Rubisco activation and mitochondrial respiration with varying temperature were considered in addition to the input data used for A_{Rubisco} . Rubisco activation responses to temperature for the C₃-cool and the C₃-warm were taken from *Deschampsia antarctica* and *Larrea tridentata*, respectively (Salvucci and Crafts-Brandner 2004). Mitochondrial respiration rates at the different temperatures were taken from *Acer saccharum* (Niinemets and Tenhunen 1997) for both C₃-cool and C₃-warm modeling

Table 1. Temperature dependence parameters of the Rubisco maximum carboxylase turnover rate (k_{cat}^c).

Group	Species	Reference for k_{cat}^c	c	ΔH_a (kJ mol ⁻¹)	ΔH_d (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	T_{opt} (°C)	T_{growth} (°C)	Reference for T_{growth}	$S_{c/o}$ (mol mol ⁻¹)	Reference for $S_{c/o}$
Archaea	<i>Thermococcus kodakariensis</i>	Ezaki et al. (1999)	15.2	37.1	284.3	765.9	90.7	85	Ezaki et al. (1999)		
Proteobacteria	<i>Chromatium tepidum</i>	Heda and Madigan (1988)	18.0	44.0	360.7	1092.7	52.1	50	Heda and Madigan (1988)		
	<i>Chromatium vinosum</i>	Heda and Madigan (1988)	23.0	57.9	387.8	1233.9	37.5	30	Heda and Madigan (1988)	53	Jordan and Chollet (1985)
	<i>Thiobacillus</i> sp. (endosymbiont of <i>Alviniconcha hessleri</i>)	Stein and Felbeck (1993)	16.3	39.7	96.8	309.4	36.7	25	Stein and Felbeck (1993)		
	<i>Thiobacillus thyasiris</i>	Cook et al. (1991)	16.9	42.0	228.8	683.8	55.4	30	Cook et al. (1991)		
Rhodophyta	<i>Cyanidium caldarium</i>	Ford (1979)	30.8	76.3	145.0	452.0	48.3	57	Ford (1979)	225	Uemura et al. (1997)
Cyanobacteria	<i>Anabaena variabilis</i>	Badger (1980)	23.1	57.3				35	Badger (1980)	31	Somerville (1986)
	<i>Synechococcus lividus</i>	Sheridan and Ulik (1976)	14.2	35.2	240.3	715.7	55.8	45	Sheridan and Ulik (1976)	46	Madgwick et al. (1998)
	<i>Synechococcus</i> strain a-1	Yaguchi et al. (1992)	11.5	27.8	540.9	1582.9	63.4	60	Yaguchi et al. (1992)	31	Yaguchi et al. (1996)
Chlorophyta (green algae)	<i>Chlamydomonas reinhardtii</i>	Devos et al. (1998)	9.9	24.4	325.4	986.3	49.9	25	Devos et al. (1998)	60	Spreitzer et al. (2005)
	<i>Chlorella emersonii</i>	Ford (1979)	11.7	29.0	157.8	498.2	35.9	25	Ford (1979)	31 ^a	Kent and Tomani (1984)
	<i>Chloromonas</i> strain ANT1	Devos et al. (1998)	10.7	26.4	491.5	1483.3	52.9	8	Devos et al. (1998)		
	<i>Chloromonas</i> strain ANT3	Devos et al. (1998)	10.9	26.9	243.0	738.1	48.6	4	Devos et al. (1998)		
Spermatophyta (C ₃ plants from cool habitats)	<i>Alopecurus alpinus</i>	Tieszen and Sigurdson (1973)	25.2	62.5	202.0	620.7	48.8	15*	Tieszen (1973)		
	<i>Arctagrostis latifolia</i>	Tieszen and Sigurdson (1973)	20.4	50.5	220.4	673.8	49.1	15*	Tieszen (1973)		
	<i>Atriplex glabriuscula</i>	Badger and Collatz (1977)	28.0	69.3				20*	¹		
	<i>Chenopodium album</i>	Sage et al. (1995)	21.3	52.9				20*	Sage et al. (1995)	79	Kane et al. (1994)
	<i>Dupontia fisheri</i>	Tieszen and Sigurdson (1973)	22.5	55.8	380.0	1153.7	51.9	15*	Tieszen (1973)		
	<i>Espeletia schultzii</i>	Castrillo (1995)	18.2	45.1				20*	Castrillo (1995)		

	<i>Pinus sylvestris</i>	Gezelius (1975)	23.2	57.3	417.8	1267.4	52.5	21	Junttila (1986)		
	<i>Poa arctica</i>	Sage et al. (2002)	24.3	60.1				15*	Sage et al. (2002)		
	<i>Poa pratensis</i>	Sage et al. (2002)	20.5	50.8				20*	Sage et al. (2002)		
	<i>Solanum tuberosum</i>	Sage et al. (2002)	22.0	54.6				22	Geigenberger et al. (1998)		
	<i>Spinacia oleracea</i>	Badger and Andrews (1974)	18.5	46.2				16	²	88	Jordan and Ogren (1984)
	<i>Triticum aestivum</i>	Makino et al. (1988)	23.4	58.1				20	Porter and Gawith (1999)	107	Parry et al. (1989)
Spermatophyta (C ₃ plants from warm habitats)											
	<i>Agropyron smithii</i>	Monson et al. (1982)	22.0	54.7				25	Read et al. (1997)	99 ^b	Kent and Tomani (1984)
	<i>Arachis hypogaea</i>	Sage et al. (2002)	24.4	60.6				30	De Beer (1963)		
	<i>Astragalus flavus</i>	Weber et al. (1977)	34.0	84.4	227.3	684.8	56.7	30*	Weber et al. (1977)		
	<i>Astragalus rafaelsensis</i>	Weber et al. (1977)	31.8	78.8	204.1	611.1	58.7	30*	Weber et al. (1977)		
	<i>Capsicum chinense</i>	Sage et al. (2002)	22.0	54.5				25	An et al. (2011)		
	<i>Flaveria pringlei</i>	Sage et al. (2002)	20.4	50.4				30*	Sage et al. (2002)	81	Kubien et al. 2008)
	<i>Glycine max</i>	Bowes et al. (1972)	19.3	47.7	280.8	853.7	50.7	25	Zhang et al. (1996)	82	Jordan and Ogren (1981)
	<i>Gossypium hirsutum</i>	Sage et al. (2002)	24.0	59.4				30*	³		
	<i>Nicotiana tabacum</i>	Crafts-Brandner and Salvucci (2000)	20.8	51.0				25	⁴	82	Whitney et al. 2009)
	<i>Oryza sativa</i>	Makino et al. (1988)	24.3	60.3				25	⁵	85	Kane et al. (1994)
	<i>Pueraria lobata</i>	Sage et al. 2002)	25.8	63.8				26	De Pereira-Netto et al. (1998)		
	<i>Solanum lycopersicum</i>	Weber et al. (1977)	29.4	72.8	157.5	480.2	54.0	30	Paul et al. (1984)	82	Jordan and Ogren (1983)
	<i>Stanleya pinnata</i>	Weber et al. (1977)	31.5	78.1	229.2	688.5	57.0	25*	Sabbagh and Van Hoewyk (2012)		
	<i>Trifolium repens</i>	Lehnher et al. (1985)	34.7	86.1				25*	⁶	73	Lehnher et al. (1985)
Spermatophyta (C ₄ plants)											
	<i>Amaranthus retroflexus</i>	Sage et al. (2002)	24.3	60.4				30*	⁷	82 ^c	Jordan and Ogren (1981)
	<i>Andropogon gerardii</i>	Tieszen and Sigurdson (1973)	20.8	51.8	254.3	776.8	49.6	30*	Tieszen (1973)		
	<i>Bouteloua gracilis</i>	Pittermann and Sage (2000)	20.8	51.8				30*	Pittermann and Sage (2000)		
	<i>Cynodon dactylon</i>	Sage et al. (2002)	21.1	52.3				30*	⁸		
	<i>Digitaria sanguinalis</i>	Sage et al. (2002)	18.8	46.6				30*	King and Oliver (1994)		
	<i>Flaveria trinervia</i>	Sage et al. (2002)	20.3	50.4				30*	Sage et al. (2002)	77	Kubien et al. 2008)
	<i>Muhlenbergia montana</i>	Sage et al. (2002)	21.2	52.7				26	Pittermann and Sage (2001)		
	<i>Portulaca oleracea</i>	Sage et al. (2002)	21.7	53.7				30	Sage et al. (2002)		
	<i>Sorghum bicolor</i>	Tieszen and Sigurdson	23.5	58.1	206.6	629.4	51.0	30	⁹	91	Badger and Andrews (1987)

Abbreviations: c , scaling constant; ΔH_a , activation energy; ΔH_d , de-activation energy; ΔS , entropy term (Eqs. 1 and 2); and T_{opt} , optimum temperature (Eq. 3). Species were assigned into six phylogenetic groups. One phylogenetic group – Spermatophyta – was further divided among C_3 and C_4 species, and C_3 species were further divided among warm and cool temperature species according to their optimum growth temperature. The optimum growth temperature values (T_{growth}) for each species were either obtained from the reference literature or assigned according to their climate of origin. The latter estimates are denoted by asterisks. The following references were obtained from internet sites:

¹<http://ib.berkeley.edu/courses/ib151/IB151Lecture6.pdf>

²<http://www.darrolshillingburg.com/GardenSite/NewsletterPDF/Spinach.pdf>

³<http://www.prota4u.info/protav8.asp?h=M4&t=Gossypium&p=Gossypium+hirsutum>

⁴http://www.fao.org/nr/water/cropinfo_tobacco.html

⁵<http://www.fao.org/ag/agp/AGPC/doc/gbase/data/pf000274.htm>

⁶<http://www.fao.org/ag/agp/AGPC/doc/Gbase/data/pf000350.htm>

⁷[http://c.ymcdn.com/sites/www.echocommunity.org/resource/collection/E66CDFDB-0A0D-4DDE-8AB1-74D9D8C3EDD4/Amaranth Grain & Vegetable Types %5bOffice Format%5d.pdf](http://c.ymcdn.com/sites/www.echocommunity.org/resource/collection/E66CDFDB-0A0D-4DDE-8AB1-74D9D8C3EDD4/Amaranth_Grain_&Vegetable_Types_%5bOffice_Format%5d.pdf)

⁸http://en.wikipedia.org/wiki/Cynodon_dactylon

⁹<http://www.fao.org/ag/agp/agpc/doc/gbase/data/pf000319.htm>

The cool-temperature C₃ species were defined as those with $T_{\text{growth}} < 25$ °C, and the warm-temperature species as those with $T_{\text{growth}} \geq 25$ °C.

Values for the Rubisco specificity factor ($S_{\text{c/o}}$) are also shown when available from literature. Original papers are indicated for the k_{cat} , T_{growth} and $S_{\text{c/o}}$ data. ^a Data for *Chlorella pyrenoidosa*; ^b data for *Agropyron intermedium*; ^c data for *Amaranthus hybridus*.

Table 2. Average temperature dependence parameters of the Rubisco maximum carboxylase turnover rate (k_{cat}) for each species group.

Group	c	ΔH_a (kJ mol ⁻¹)	ΔH_d (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	T_{opt} (°C)	T_{growth} (°C)	$S_{\text{c/o}}$
Archaea	15.2	37.2	284	766	90.7	85	
Proteobacteria	18.5 ± 1.5	45.9 ± 4.1	269 ± 67	830 ± 209	45.4 ± 4.9	33.8 ± 5.5	53.0
Rhodophyta	30.8	76.3	145	452	48.3	57	225.0
Cyanobacteria	16.3 ± 3.5	40.1 ± 8.9	391 ± 150	1149 ± 434	59.6 ± 3.8	46.7 ± 7.3	36.0 ± 5.1
Chlorophyta	10.8 ± 0.4	26.7 ± 0.9	304 ± 71	927 ± 211	46.8 ± 3.8	15.5 ± 5.5	45.5 ± 14.5
Spermatophyta	23.5 ± 0.7	58.1 ± 1.7	253 ± 24	767 ± 72	52.7 ± 1.0	24.7 ± 0.9	85.1 ± 2.6
Spermatophyta C ₃ -cool	22.3 ± 0.8 ^a	55.3 ± 2.0 ^a	305 ± 55	929 ± 165	50.6 ± 1.0 ^a	18.3 ± 0.8 ^a	91.2 ± 8.3
Spermatophyta C ₃ -warm	26.0 ± 1.4 ^b	64.5 ± 3.5 ^b	220 ± 20	664 ± 61	55.4 ± 1.4 ^b	27.2 ± 0.7 ^b	83.4 ± 3.0
Spermatophyta C ₄	21.3 ± 0.5 ^a	52.8 ± 1.3 ^a	231 ± 24	703 ± 74	50.3 ± 0.7 ^a	29.6 ± 0.4 ^b	83.0 ± 3.8

Abbreviations: c , scaling constant, ΔH_a , activation energy; ΔH_d , de-activation energy; ΔS , entropy term (Eqs. 1 and 2); and T_{opt} , optimum temperature (Eq. 3); optimum growth temperature (T_{growth}); and $S_{\text{c/o}}$, Rubisco specificity factor. Data are means ± S.E., except when $n = 1$. Within Spermatophyta, significant differences among C₃-cool, C₃-warm (Table 1 for the definition) and C₄ species ($P < 0.05$ according to one-way ANOVA followed by Duncan test) are denoted by different letters.

Table 3. Correlations of phylogenetically independent contrasts (PicR) among the parameters of the temperature response curve of Rubisco carboxylase maximum turnover rate (k_{cat}°), Rubisco specificity factor ($S_{\text{c/o}}$) and the optimum temperature for the growth of the organism (T_{growth}) for all species together (A, $n = 49$), for unicellular aquatic organisms (Archaea, Proteobacteria, green and red algae (B); $n = 13$), for all Spermatophyta – plants (C, $n = 36$) and for C_3 plants only (D, $n = 26$).

(A)	ΔH_a	ΔH_d	ΔS	T_{opt}	$S_{\text{c/o}}$	T_{growth}
c	1.000	-0.111	-0.094	0.005	0.338	0.019
ΔH_a		-0.113	-0.095	0.001	0.334	0.007
ΔH_d			0.999	0.824	0.267	0.278
ΔS				0.716	0.260	0.272
T_{opt}					0.303	0.124
$S_{\text{c/o}}$						0.754
(B)	ΔH_a	ΔH_d	ΔS	T_{opt}	$S_{\text{c/o}}$	T_{growth}
c	0.999	-0.443	-0.415	-0.493	0.559	0.017
ΔH_a		-0.442	-0.413	-0.496	0.549	-0.001
ΔH_d			0.998	0.649	-0.065	0.252
ΔS				0.493	-0.070	0.241
T_{opt}					0.069	0.212
$S_{\text{c/o}}$						0.591
(C)	ΔH_a	ΔH_d	ΔS	T_{opt}	$S_{\text{c/o}}$	T_{growth}
c	1.000	-0.179	-0.158	0.288	0.361	0.341
ΔH_a		0.183	0.163	0.290	0.353	0.331
ΔH_d			0.999	0.882	0.345	0.125
ΔS				0.744	0.332	0.117
T_{opt}					0.447	0.037
$S_{\text{c/o}}$						0.898
(D)	ΔH_a	ΔH_d	ΔS	T_{opt}	$S_{\text{c/o}}$	T_{growth}
c	1.000	-0.202	-0.180	0.274	0.263	0.242

ΔH_a	0.204	0.182	0.275	0.265	0.244
ΔH_d		<i>0.999</i>	<i>0.888</i>	<i>0.588</i>	<i>0.378</i>
ΔS			<i>0.743</i>	<i>0.581</i>	<i>0.382</i>
T_{opt}				<i>0.613</i>	0.051
$S_{c/o}$					<i>0.942</i>

Abbreviations: c , scaling constant, ΔH_a , activation energy; ΔH_d , de-activation energy; ΔS , the entropy term; T_{opt} , the optimum temperature of the Rubisco maximum carboxylase turnover rate. Values in bold italics are significant ($P < 0.05$).

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.