1   **Title:** Macromolecular Rate Theory (MMRT) Provides a Thermodynamics Rationale to Underpin the

2   Convergent Temperature Response in Plant Leaf Respiration

3   **Running Title**: MMRT explains thermal response of respiration

4   **Authors**: Liyin L. Liang[1*], Vickery L. Arcus[1], Mary A. Heskel[2,3], Odhran S. O'Sullivan[2,4], Lasantha K.

5   Weerasinghe[2,5], Danielle Creek[2,6], John JG Egerton[2], Mark G. Tjoelker[6], Owen K. Atkin[2,7], Louis A.

6   Schipper[1*]

7   **Affiliations:**

8   [1] School of Science, The University of Waikato, Hamilton 3240, New Zealand

9   [2] Division of Plant Sciences, Research School of Biology, The Australian National University, Canberra,

10   ACT 2601, Australia

11   [3] The Ecosystems Center, Marine Biological Laboratory, Woods Hole, MA 02543, USA

12   [4] Animal and Plant Sciences, The University of Sheffield, Sheffield, S10 2TN United Kingdom

13   [5] Faculty of Agriculture, University of Peradeniya, Peradeniya, 20400 Sri Lanka

14   [6] Hawkesbury Institute for the Environment, Western Sydney University, Penrith, NSW 2751, Australia

15   [7] ARC Centre of Excellence in Plant Energy Biology, Research School of Biology, The Australian

16   National University, Canberra, ACT 2601, Australia

17   **Corresponding Authors:**

18   Liyin L. Liang, School of Science, The University of Waikato, Hamilton 3240, New Zealand (tel: +64 7

19   8386229, fax: +64 8560115, email: lssllyin@gmail.com)

20   Louis A. Schipper, School of Science, The University of Waikato, Hamilton 3240, New Zealand (tel: +64

21   7 8384468, fax: +64 8560115, e-mail: louis.schipper@waikato.ac.nz)

22   **Keywords**: MMRT   Heat Capacity   Temperature Response   Thermodynamics   Leaf Respiration

23   Climate Change   Arrhenius

24   **Type of article:** Primary Research Articles

25

26   **Abstract:** Temperature is a crucial factor in determining the rates of ecosystem processes, e.g. leaf

27   respiration (R) − the flux of plant respired CO_2 from leaves to the atmosphere. Generally, R increases

28   exponentially with temperature and formulations such as the Arrhenius equation are widely used in earth

29   system models. However, experimental observations have shown a consequential and consistent

30   departure from an exponential increase in R. What are the principles that underlie these observed

31   patterns? Here, we demonstrate that macromolecular rate theory (MMRT), based on transition state

32   theory for enzyme-catalyzed kinetics, provides a thermodynamic explanation for the observed departure

33   and the convergent temperature response of R using a global database. Three meaningful parameters

34   emerge from MMRT analysis: the temperature at which the rate of respiration would theoretically reach a

35   maximum (*the optimum temperature, T_{opt}*), the temperature at which the respiration rate is most sensitive

36   to changes in temperature (*the inflection temperature, T_{inf}*) and the overall curvature of the log(rate)

37   versus temperature plot (*the change in heat capacity for the system*, $\Delta C_P^{\ddagger}$). On average the highest

38   potential enzyme-catalyzed rates of respiratory enzymes for R is predicted to occur at 67.0±1.2 °C and the

39   maximum temperature sensitivity at 41.4±0.7 °C from MMRT. The average curvature (average

40   negative $\Delta C_P^{\ddagger}$) was -1.2±0.1 kJ.mol^{-1}K^{-1}. Interestingly, T_{opt}, T_{inf} and $\Delta C_P^{\ddagger}$ appear insignificantly different

41   across biomes and plant functional types (PFTs), suggesting that thermal response of respiratory enzymes

42   in leaves could be conserved. The derived parameters from MMRT can serve as thermal traits for plant

43   leaves that represents the collective temperature response of metabolic respiratory enzymes and could be

44   useful to understand regulations of R under a warmer climate. MMRT extends the classic transition state

45   theory to enzyme-catalyzed reactions and provides an accurate and mechanistic model for the short-term

46   temperature response of R around the globe.

Introduction

Leaf respiration (R) contributes c.30 Pg (30 billion metric tons) carbon per year to the atmosphere (Prentice *et al.*, 2001; Canadell *et al.*, 2007; IPCC, 2013), about 4 times higher than the industrial CO_2 emissions (~8 Pg C yr^{-1}) between 2002 to 2011 (IPCC the fifth assessment report Table 6.1, chapter 6 (Ciais *et al.*, 2013)). Consequently, small changes in R have the potential to make a huge impact on the atmospheric CO_2 concentrations. It is generally predicted that R will increase with the increasing mean global temperature from the current earth system model projections. Increases in R are not linear with temperature but rather exponential as modelled by the Arrhenius equation. However, departures from Arrhenius behaviour are well known for many biologically driven reactions such as leaf respiration, photosynthesis and soil carbon decomposition (Lloyd & Taylor, 1994; Tjoelker *et al.*, 2001; Alster *et al.*, 2016; Ma *et al.*, 2017; Robinson *et al.*, 2017).

In a recent study, Heskel *et al.* (2016b) reported a universal convergence in temperature response of R across different biomes and plant functional types (PFTs) using a global dataset of plant leaf respiration measurements. They demonstrated a consistent curvature in log-transformed R vs temperature plots that was best fit using a second-order log-polynomial model (LP model) for a large number of R versus temperature datasets. They compared the LP model to four other conventional models (exponential fixed-Q_{10}, Arrhenius, Lloyd & Taylor and variable-Q_{10}) and showed improved predictive power in estimating the carbon release from vegetation. An modified Arrhenius model with 3 components, which describes the temperature dependence of activation energy in Arrhenius model as a second-order polynomial function, also provides equivalent fits as the LP model (Kruse & Adams, 2008; Kruse *et al.*, 2011; Adams *et al.*, 2016; Heskel *et al.*, 2016a). Since respiratory metabolism in a leaf involves a series of enzyme-catalyzed reactions, via the tricarboxylic acid (TCA) cycle or cytochrome pathways (Buchanan *et al.*, 2015), a mechanistic underpinning of the temperature response of R may be found in the temperature dependence of enzyme-catalyzed reaction rates.

We have recently developed macromolecular rate theory (MMRT), which extends the classic transition state theory for the temperature dependence of chemical reactions to those reactions catalyzed by

3

73   enzymes (large macromolecules, hence the MMRT name) (Hobbs *et al.*, 2013; Arcus *et al.*, 2016). We

74   have also applied MMRT to complex biological systems such as soil processes to describe their

75   temperature dependence, e.g., soil carbon decomposition, nitrification, denitrification, methanogenesis

76   and soil respiration (Schipper *et al.*, 2014; Robinson *et al.*, 2017). MMRT has recently been applied by

77   other groups to soil enzymes and microbial processes in soil (Alster *et al.*, 2016) and has been used to

78   distinguish between nitrifying archaea and bacteria (Taylor *et al.*, 2016). In all of these studies, MMRT

79   captures the curvature in the log(rate) versus temperature plots without invoking enzymatic denaturation.

80   Here, we show that MMRT also models the short-term temperature dependence of *R* with predictive

81   power equivalent to the LP model defined by Heskel *et al.* (2016b). Indeed, we show that the two models

82   are nearly equivalent mathematically. Specifically, we use the large *R* dataset collected by Heskel and

83   colleagues to compare the performance of Arrhenius, MMRT and LP models in describing the

84   temperature response of *R*. We argue that whilst the LP model provides excellent empirical predictions

85   with respect to *R*, the MMRT model goes a step further in determining parameters that have a basis in

86   thermodynamics and thus, meaningful interpretation when comparing the temperature dependence of

87   different ecosystem processes at differing scales.

88   **Materials and methods**

89   *R measurements*

90   We used the dataset provided by Heskel *et al*. (2016b), which included 673 individual temperature

91   response curves of *R* across 231 species, 18 sites, 7 biomes and 7 plant functional types (PFTs). Details

92   of the field sites, species, biomes, PFTs and protocols for measurement of CO_2 exchange between leaf

93   and atmosphere are provided in Heskel *et al.* (2016b). In the current study, for consistency, we used

94   respiration data measured up to 45 °C.

95   *Development of MMRT*

96   Chemical, biological and ecological modellers have long used the Arrhenius function to describe the

97   relationship between temperature and the reaction rate: $k=A \exp(-E_a/RT)$, where the *k* is the rate constant,

98   *A* is the pre-exponential factor, E_a is the activation energy, *R* is the gas constant and *T* is temperature (K).

4

99   The central concept invoked by the Arrhenius function is the activation energy (E_a) for a reaction which is

100   defined as the energy barrier between the ground state and transition state for a given reaction. Eyring,

101   Evans, Polanyi and others extended the Arrhenius function to develop Transition State Theory (TST) that

102   provides a statistical thermodynamic description of the pre-exponential factor (A) and defines E_a as the

103   difference in Gibbs free energy between the ground state and transition state ($\Delta G^{\ddagger}$). Further, it is

104   generally assumed that the temperature dependence of $\Delta G^{\ddagger}$ is described by the Gibbs equation, $\Delta G^{\ddagger}=\Delta H^{\ddagger}$

105    $- T\Delta S^{\ddagger}$, where $\Delta H^{\ddagger}$ is the change in enthalpy, and $\Delta S^{\ddagger}$ is the change in entropy, between the ground state

106   and the transition state for the reaction. Hence, the Eyring equations and their equivalent log forms are:

107
$$k = \frac{\kappa k_B T}{h} e^{\left(\frac{-\Delta G^{\ddagger}}{RT}\right)}, \quad \ln(k) = \ln\left(\frac{\kappa k_B T}{h}\right) - \frac{\Delta G^{\ddagger}}{RT} \tag{1}$$

108
$$k = \frac{\kappa k_B T}{h} e^{\left[\frac{-\left(\Delta H^{\ddagger}-T\Delta S^{\ddagger}\right)}{RT}\right]}, \quad \ln(k) = \ln\left(\frac{\kappa k_B T}{h}\right) - \left[\frac{\left(\Delta H^{\ddagger}-T\Delta S^{\ddagger}\right)}{RT}\right] \tag{2}$$

109   where κ, k_B, h and R refer to the transmission coefficient (here, κ is assumed to be 1 for simplicity),

110   Boltzmann and Planck's constants, and the universal gas constant, respectively. Similarly, it is generally

111   assumed that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are independent of temperature and this assumption holds for the vast majority

112   of chemical reactions involving small molecules in standard solvents. However, in biological systems

113   when enzymes (macromolecules) are involved in the reactions, this assumption no longer holds and we

114   must consider the change in heat capacity ($\Delta C_P^{\ddagger}$) for the reaction (formally, the temperature dependence of

115   the enthalpy and entropy for the reaction). The $\Delta C_P^{\ddagger}$ has been shown to be important in enzyme catalysis

116   (Arcus & Pudney, 2015; Arcus *et al.*, 2016). This leads to an expansion of equation (2) above to give the

117   MMRT equation:

118
$$\ln(k) = \ln\left(\frac{k_B T}{h}\right) - \frac{\left(\Delta H_{T_0}^{\ddagger}+\Delta C_P^{\ddagger}(T-T_0)\right)}{RT} + \frac{\left(\Delta S_{T_0}^{\ddagger}+\Delta C_P^{\ddagger}(lnT-lnT_0)\right)}{R} \tag{3}$$

119   where T_0 is a suitable reference temperature and $\Delta C_P^{\ddagger}$ is the change in heat capacity between the ground

120   state and the transition state for the enzyme-catalyzed reaction. Although the MMRT function appears

121   complicated, it is nothing more than a theoretical parameterization of the pre-exponential term (*A*) and the

122   activation energy (E_a) from the familiar Arrhenius function. If there is no heat capacity change during the

123   reaction (i.e., $\Delta C_P^{\ddagger} = 0$), MMRT simply collapses to the Arrhenius and Eyring equations (Hobbs *et al.*,

124   2013; Arcus *et al.*, 2016). Notably, the Arrhenius function has two unknowns (A and E_a) and the MMRT

125   function has three unknowns ($\Delta H_{T_0}^{\ddagger}$, $\Delta S_{T_0}^{\ddagger}$ and $\Delta C_P^{\ddagger}$). However, $\Delta H_{T_0}^{\ddagger}$ and $\Delta S_{T_0}^{\ddagger}$ are tightly correlated due to

126   the so called enthalpy-entropy compensation (Fig. S1) and hence, adding a third parameter does not

127   simply improve the fit to the data *ad hoc*. Indeed, the log-polynomial function used by Heskel and

128   colleagues has three *independent* unknowns (the coefficients, *a*, *b*, and *c*). Additionally, the $\Delta S_{T_0}^{\ddagger}$ in

129   MMRT captures the magnitude change of reaction rate caused by substrate concentrations.

130   The temperature dependence of enzyme-catalyzed rates typically shows an exponential rise with

131   temperature up to an optimum temperature above which the rate declines. The textbook explanation for

132   the decline in rate at high temperatures is denaturation of the enzyme leading to its inactivation.

133   However, it has been demonstrated in very many cases that this does not account for either the optimum

134   temperature (T_{opt}) or curvature in the log(rate) versus temperature plots for temperatures below T_{opt}

135   (Thomas & Scopes, 1998; Buchanan *et al.*, 1999; Daniel & Danson, 2010; Hobbs *et al.*, 2013). We have

136   shown that enzyme-catalyzed rates proceed with a measurable $\Delta C_P^{\ddagger}$ and that the curvature below T_{opt} and

137   the position of both T_{opt} and an inflexion point T_{inf} can be deduced from MMRT and the important

138   parameter $\Delta C_P^{\ddagger}$ (Hobbs *et al.*, 2013; Arcus *et al.*, 2016) (see Text S1 for details about the derived

139   parameters T_{opt} and T_{inf} from MMRT).

140   *The mathematical connection between MMRT and the LP model*

141   Heskel *et al.* (2016b) plot the log of the rate versus temperature for leaf respiration and fit a second order

142   polynomial to the data showing excellent convergence of the polynomial coefficients across ecosystems

143   and plant functional types (the coefficients *b* & *c* converge, the third coefficient, *a*, determines the

144   absolute amplitude of the rate at a reference temperature which varies between species and climates).

145    $\ln(k) = a + bT + cT^2$ (4)

146   We have also fitted the MMRT function to these data and find a similar convergence of the MMRT

147   parameters (see next section for details). This suggested to us that the LP function and MMRT are

148   mathematically closely related (Fig. 1) and this turns out to be the case.

149   A Taylor expansion for Eq (1) around a suitable reference temperature T_0 gives (see Text S2 for the

150   deduction):

151    $\ln(k) = ln\left(\frac{k_B T_0}{h}\right) - \frac{\Delta G_{T_0}^{\ddagger}}{RT_0} + \left(\frac{1}{T_0} + \frac{\Delta H_{T_0}^{\ddagger}}{RT_0^2}\right)(T - T_0) + \left(\frac{\Delta C_P^{\ddagger}}{2RT_0^2}\right)(T - T_0)^2$ (5)

152   The first two terms are a constant and may be combined as coefficient *a* in Eq (4) above. Importantly,

153   these terms define the rate at the reference temperature and encapsulate all of the variables that contribute

154   to that rate (e.g., substrate availability, activation energy at T_0, moisture availability, etc.). This is the

155   amplitude term and in keeping with Heskel and colleagues, we will call this *a*(MMRT). The second two

156   terms constitute the linear coefficient of T (equivalent to coefficient *b* in Eq (4) above). The last term is

157   the quadratic term (coefficient *c* in Eq (4) above). Thus, Eq (4) used by Heskel *et al*. (2016b) can be

158   rewritten as:

159    $\ln(k) = a + b(T - T_0) + c(T - T_0)^2$ (6)

160   Hence the correspondence between MMRT and the LP function is:

161    $a = ln\frac{k_B T_0}{h} - \frac{\Delta G_{T_0}^{\ddagger}}{RT_0}, \quad b = \frac{1}{T_0} + \frac{\Delta H_{T_0}^{\ddagger}}{RT_0^2}, \quad c = \frac{\Delta C_P^{\ddagger}}{2RT_0{}^2}$ (7)

162   Thus, the amplitude term, *a* is simply Eqs 1&5 at the reference temperature T_0. The linear term (*b*) is a

163   function of the change in enthalpy for the reaction at the reference temperature ($\Delta H_{T_0}^{\ddagger}$) and the quadratic

164   term (*c*) is a function of the change in heat capacity for the reaction ($\Delta C_P^{\ddagger}$) and defines the "curvature" of

165   the rate versus temperature.

166   *Curve fitting and statistics*

167   In this study, we fitted the leaf respiration rate versus temperature datasets using Arrhenius, MMRT and

168   LP functions to retrieve the estimated parameters from each model. Before fitting the data, we checked

169   each individual ln*R*-T curve manually by plotting in Matlab (2015a (The MathWorks Inc., Natick, MA,

170   USA). In several cases we identified an unexplained upward rise in respiration rate at low temperatures

171   (below ~10 °C). This low temperature hook may be due to the measurement protocols in leaf respiration

172   where the temperature adjustment period was insufficiently long to fully cool the leaves before

173   temperature began to increase in the cuvette. About 7% of the ln$R$-T dataset curves showed this

174   phenomenon and to minimize the effects of this artefact on the fitted parameters, we fitted measurements

175   to data above this low temperature using Arrhenius, LP and MMRT functions.

176   For each curve-fitting run, the parameters (Arrhenius pre-exponential factor, A, and activation energy

177   E_a; MMRT, $\Delta H^{\ddagger}_{T_0}$, $\Delta S^{\ddagger}_{T_0}$ and $\Delta C^{\ddagger}_{P}$; LP coefficients, a, b and c) were not constrained. The T_0 was set to

178   298.15 K (25 °C) as a reference temperature. The curve was fitted using the *nlinfit* function of MATLAB

179   2015a (The MathWorks Inc., Natick, MA, USA). We conducted 1000-iteration bootstrapping with

180   sample replacement to retrieve the estimated parameters from three models. At each bootstrapping run,

181   we constrained 75% of the data in each lnR-T curve since more data results in higher confidence in

182   parameter estimates (Robinson *et al.*, 2017). We use the medians of the 1000-iteration bootstrapped

183   parameters to represent the best estimates. For model comparisons among three models, we further

184   calculated the corrected Akaike Information Criterion (AICc) value to assess the performance of the three

185   models. AICc provides a measure for model comparison and suggests that a model showing a smaller

186   AICc value is better. We used 3 parameters in MMRT and LP models and 2 parameters for the Arrhenius

187   function to calculate the AICc. We applied one-way ANOVA to test the difference of the calculated

188   AICc among three models across 673 curves.

189   Mean parameter values of each species for MMRT, i.e., $\Delta H^{\ddagger}_{T_0}$, $\Delta S^{\ddagger}_{T_0}$ and $\Delta C^{\ddagger}_{P}$, were calculated,

190   including 231 species in 673 individual measurements across the global dataset. We further calculated

191   T_{opt} and T_{inf} only when they were within the biological range (298.15-373.15K, 25-100 °C). The mean

192   a(MMRT), $\Delta H^{\ddagger}_{T_0}$, $\Delta C^{\ddagger}_{P}$, T_{opt} and T_{inf} were statistically compared across 7 biomes and 7 plant functional

193   types (PFTs) using mixed effect model as Heskel *et al.* (2016b). The Tukey's honestly significant

194   difference (HSD) test was used to conduct the *post hoc* intra-group comparisons.

Results

Comparisons between fits using Arrhenius, MMRT and LP equations

All three models, Arrhenius (Eq.1), MMRT (Eq.3) and LP (Eq.6) were able to describe the temperature

response of R (Fig. 2a), although it is clear from the residuals that the MMRT and LP models outperform

the Arrhenius function (Fig. 2b). ANOVA of AICc among 3 models also showed that both MMRT and

LP models were consistently better than the Arrhenius model in predicting the temperature response of R

across 673 individual ln$R$-T curves, with statistically significant lower AICc ($p<0.0001$) values from both

MMRT and LP models compared to the Arrhenius function (Fig. 2c). This conclusion is consistent with

the results of Heskel *et al.* (2016b), who demonstrated that the LP model better characterized the

temperature response of R when compared to four other Arrhenius-based models. MMRT provided

equivalent predictive power for the temperature response of R when compared to the empirical LP model

since there was no statistical difference among AICc values ($p=0.99$) between MMRT and LP models.

This is unsurprising given the near equivalence of the mathematical functions for the MMRT and LP

models or a modified Arrhenius model proposed by Adams *et al.*(2016).

Bridging MMRT and polynomial models

The parameters derived from fits between the LP and MMRT models are nearly identical (Fig. 3). The R

value at T_0 (298.15K, 25°C), i.e., parameter a in the LP model, is almost the same as that calculated from

MMRT at T_0 (Fig. 3a**)**, with an inconsequential difference between a and R at T_0 (a-R_{25}) of -0.0011 µmol

CO_2 m^{-2} s^{-1}. Parameter b in the LP model, is commensurate with that from MMRT (Fig. 3b**)**, with a

difference of 9.1×10^{-5} µmol CO_2 m^{-2} s^{-1} K^{-1}. The curvature term between MMRT and LP is also equivalent

(Fig. 3c). The difference between c and $\Delta C_P^{\ddagger} / 2RT_0^2$ is -2.2×10^{-4} µmol CO_2 m^{-2} s^{-1} K^{-2}, which is equivalent

to a difference of -0.3 kJ mol^{-1} K^{-1} in $\Delta C_P^{\ddagger}$. Thus, MMRT and LP functions both model R equally (Fig. 1)

and provide closely comparable parameters, suggesting that we can either use MMRT or the LP function

to characterize the temperature response of R.

MMRT explains the temperature response of R

220   MMRT provides three biologically meaningful parameters: the temperature at which the rate of respiration

221   is predicted to reach maximum rates (the so called *optimum temperature, T_{opt}*), the temperature at which

222   the respiration rate is most sensitive to changes in temperature (the *inflection temperature*, T_{inf}) and the

223   overall curvature of the ln$R$-T curve (the so called *change in heat capacity* for the system, $\Delta C_P^\ddagger$). The T_{opt}

224   and T_{inf} are a function of $\Delta C_P^\ddagger$ and $\Delta H_{T_0}^\ddagger$ (See Text S1). $\Delta G_{T_0}^\ddagger$ ($\Delta G_{T_0}^\ddagger = \Delta H_{T_0}^\ddagger - T_0 \Delta S_{T_0}^\ddagger$) reflects the

225   magnitude of R at the reference temperature. It must be noted that many variables are rolled into $\Delta G_{T_0}^\ddagger$ and

226   it cannot be considered a true activation energy. To make this point clear, we will refer to the magnitude

227   term, the first two terms from Eq.7, as a(MMRT). The convergent MMRT parameters for temperature

228   response of R are $\Delta C_P^\ddagger$ and $\Delta H_{T_0}^\ddagger$, which are the analogues of the parameters c and b from Heskel *et al.*

229   (2016b), respectively. Accordingly, there is no significant difference in $\Delta H_{T_0}^\ddagger$ across biomes (p=0.72) and

230   plant functional types (PFTs) (p=0.60) or in $\Delta C_P^\ddagger$ (p=0.22 and p=0.24 in biomes and PFTs, respectively).

231   The global mean parameters, b and c in Heskel *et al.* (2016b), 0.1012 μmol m^{-2} s^{-1} C^{-1}and -0.0005 μmol m^{-}

232   ^{2} s^{-1} C^{-2} , are equivalent to $\Delta H_{T_0}^\ddagger$=53.8 kJ mol^{-1} and $\Delta C_P^\ddagger$=-0.7 kJ mol^{-1} K^{-1}in MMRT, respectively. The

233   results from MMRT agree with the convergent temperature response of R in Heskel *et al.* (2016) using the

234   LP model. The consequence of consistent $\Delta H_{T_0}^\ddagger$ and $\Delta C_P^\ddagger$ values leads to insignificant differences of T_{opt}

235   and T_{inf} of R across global datasets (Table 1). We found marginal differences in T_{opt} and T_{inf} across biomes

236   (p=0.07 and p=0.09) and no statistically difference across PFTs (p=0.32 and p=0.42), with mean T_{opt} and

237   T_{inf} of R 67.0 °C and 41.4 °C, respectively. While we were unable to demonstrate statistically significant

238   differences in T_{opt}, T_{inf} within biomes and PFTs, ranges in both were high (Table 1) and further work is

239   needed to determine the reasons for these large ranges.

240   In contrast, the magnitude term, a(MMRT), was significantly different between biomes (p<0.0001) and

241   PFTs (p<0.0001) (Table 1), with a decreasing trend from tundra (Tu) to tropical rainforest at low

242   elevation (TrRF_lw) and from C$_3$ herbaceous (C$_3$H) plant to broadleaf evergreen tropical (BlEvTrp)

243   plants (Table 1). Regression analysis revealed that both mean annual temperature (MAT) (R^2=0.24,

244   p=0.037) and mean annual precipitation (MAP) (R^2=0.74, p<0.0001) was correlated with a(MMRT)

245   across 18 sites at global scales(Fig. S2). Our results also identified a systematic variation in a(MMRT)

246   with water availability(Fig 4.a), showing a clear negative relationship with aridity index (R^2=0.65,

247   p<0.0001). Our result agrees with the acclimation pattern of plant respiration that shows a similar R rate

248   for plants from contrasting environments (Fig. 4b**)** (Atkin & Tjoelker, 2003; Atkin *et al.*, 2015;

249   Vanderwel *et al.*, 2015).

250   **Discussion**

251   We have compared the predictive power of MMRT, LP and Arrhenius models for characterizing the

252   temperature response of plant leaf respiration (R) using the short-term temperature-response data reported

253   by Heskel and colleagues (Heskel *et al.,* 2016b) across different biomes and plant functional types

254   (PFTs). Our results show that both MMRT and LP functions are better than the Arrhenius model in

255   characterizing the temperature response of R. These results are consistent with our expectation across

256   different biomes and PFTs from the global dataset, suggesting a convergence in temperature response of

257   R as shown by Heskel *et al.* (2016b) using the LP model. MMRT and LP models have equivalent

258   explanatory power for predicting the temperature response of R, and we have shown here the

259   mathematical equivalence between these two models. We now explore the differences and utility of the

260   MMRT and LP models.

261   The LP model is straightforward to understand and implement as it has a simple and familiar

262   mathematical form. The initial increase and then decline of R with increasing temperature is determined

263   by the curvature term, i.e., c in Eq (6), and the other 2 parameters, i.e., a and b, help to constrain the

264   magnitude and changing rate of R with temperature. From a modelling perspective, this LP model is

265   sufficient to describe the temperature response of R. However, the lack of biological meaning of the

266   fitted parameters of the LP model limits its capability to reveal the regulation of temperature response of

267   plant R. As an alternative, MMRT incorporates the central concepts of thermodynamics (activation

268   energies, enthalpy and heat capacity) which will allow insight into the determinants of respiration

269   pathways for R and potential comparison to temperature dependence of other biological processes, such

11

270   as photosynthesis and respiration by other groups of organisms, e.g., soil respiration (Robinson *et al.*,

271   2017), by characterizing their thermal properties using the changed heat capacity, $\Delta C_p^{\ddagger}$. This may allow a

272   unified understanding of the temperature response of biological processes. For example, the average

273   curvature ($\Delta C_p^{\ddagger}$ = -1.2±0.1 kJ.mol^{-1}K^{-1}) for plant respiration is significantly less than the average

274   curvature seen for heterotrophic soil respiration accurately measured in the laboratory ($\Delta C_p^{\ddagger}$ = -2.1±0.1

275   kJ.mol^{-1}K^{-1})(Robinson *et al.*, 2017).

276   MMRT may appear to have a more complicated form but it is simply the form used to model the

277   temperature dependence of enzyme-catalyzed rates. It has its roots in transition state theory (TST) which

278   is a very robust description of chemical reaction rates. Biologists and ecologists have observed

279   decreasing activities of the leaf respiratory enzymes at higher temperatures and modified the Arrhenius

280   equation to explore the mechanism by introducing a polynomial term to describe the temperature

281   dependence of activation energy (Kruse & Adams, 2008; O'Sullivan *et al.*, 2013; Noguchi *et al.*, 2015;

282   Heskel *et al.*, 2016b). We have shown that MMRT can be rearranged to a form equivalent to the LP

283   function using a 2nd-order Taylor expansion (Eq.5). MMRT also collapses to the Arrhenius (and TST)

284   function when the $\Delta C_p^{\ddagger}$ =0. It is well known that the activation energy that describes ecosystem processes

285   is temperature dependent (Lloyd and Taylor, 1994; Davidson & Janssens, 2006). MMRT accounts for

286   this temperature dependence by introducing the concept of $\Delta C_p^{\ddagger}$, the change in heat capacity between the

287   ground state and transition state of enzyme-substrate complex (Hobbs *et al.*, 2013; Arcus & Pudney,

288   2015). Formally, $\Delta C_p^{\ddagger}$ is defined as the temperature dependence of the enthalpy and entropy and thus

289   encapsulates the temperature dependence of the activation energy. The molecular origins of $\Delta C_p^{\ddagger}$ have

290   been discussed elsewhere (Arcus & Pudney, 2015; Arcus *et al.*, 2016). Briefly, the chemical meaning of

291    $\Delta C_p^{\ddagger}$ is to indicate the difficulty or the energy barrier needed to be crossed for enzyme-catalyzed reactions

292   to proceed. As a reaction gets more difficult, a higher absolute $\Delta C_p^{\ddagger}$ can be observed. $\Delta C_p^{\ddagger}$ values are

293   generally negative for enzyme-catalyzed reactions and it also can be scaled up to describe enzyme-driven

294   processes such as metabolism. Here, we demonstrate that the majority of *R* curves have negative $\Delta C_p^{\ddagger}$

295   with an average value of -1.2±0.1 kJ.mol^{-1}K^{-1} for 167 out of 231 species (70%). The consequence of a

296   negative $\Delta C_p^{\ddagger}$ is that the catalyzed rate will diverge from Arrhenius behaviour and predict an optimum

297   temperature above which rates will decline (although this predicted optimum is above observed

298   temperatures in nature). Similarly improved fits by MMRT to temperature response have also been

299   demonstrated for enzymes kinetics (Hobbs *et al.*, 2013), soil microbial extracellular enzymes (Alster *et*

300   *al.*, 2016), soil nitrification (Taylor *et al.*, 2016) and soil respiration (Schipper *et al.*, 2014; Robinson *et*

301   *al.*, 2017). Heskel *et al.* (2016b) argued for a universal convergence of temperature response of *R* using

302   the same global leaf respiration dataset and the current study shows that MMRT is also able to

303   characterize the temperature response of *R*. From the enzyme kinetic perspective, the constant observed

304     $\Delta C_p^{\ddagger}$ across the globe for leaf respiration (Table1) suggests that the contributions from metabolic enzyme

305   rates for leaf respiration across different plant species are similar, supporting the concept of a global

306   convergence of the short-term temperature response of *R* (Heskel *et al.*, 2016b).

307   Based on the short-term measurements of *R*, plants across biomes are adapted to their respective

308   environments and homeostasis of respiration could result in a similar *R* rate for plants from contrasting

309   environments (Fig. 4b) (Atkin & Tjoelker, 2003; Ow *et al.*, 2008a, 2008b; Slot & Kitajima, 2015). For

310   example, the *R* rates from tropical forests have values close to those of tundra plants (i.e. respiratory

311   homeostasis), when each is measured at their respective growth temperature (Fig. 4b). This would then

312   correspond to decreasing *a*(MMRT) from cool/dry to high temperature/humid environment (Fig. 4b). The

313   pattern of *a*(MMRT) calculated from MMRT agrees with previous findings (Atkin *et al.*, 2015;

314   Vanderwel *et al.*, 2015) which showed a clear negative relationship between *R* at reference temperature

315   and aridity index. When comparisons were made of rates of respiration at the prevailing growth

316   temperature of each site, we demonstrated a similar *R* among contrasting environments (Fig. 4b).

317   Interestingly, site-to-site variations in mean annual precipitation were more strongly correlated with

318   *a*(MMRT) than MAT, suggesting a higher *a*(MMRT) in the arid regions than those in more humid

319   climates (Fig. S2). Thus, for a given growth temperature, exposure to dry conditions is associated with

320   higher basal rates of respiration (i.e. higher *a*(MMRT)). Similarly, for a given MAP, *R* decreases with

321 increasing growth temperature. These patterns are similar to those reported by Atkin et al. (2015) in their

322 analysis of global variations in leaf respiration at a common measuring temperature of 25°C.

323 We found that the T_{opt} derived from MMRT was generally greater than the measured T_{max} (the actual

324 maximum R based on measurements reported by O'Sullivan $et\ al.$ (2017)) for the same plant species.

325 T_{max} exhibited clear biogeographic patterns with T_{max} increasing linearly from polar to equatorial regions

326 (O'Sullivan $et\ al.$, 2017). Similar patterns for T_{opt} were not found and our results suggested a relatively

327 constant T_{opt} across all the observed species from the globe (Table1). We hypothesize that the difference

328 between T_{opt} and T_{max} was due to the way these were determined and the underlying physiological

329 responses these two indices represent. T_{opt} was mathematically determined from fits of MMRT using

330 respiration measurements up to 45 °C, whereas, T_{max} was determined experimentally with leaves exposed

331 to temperatures often well above 50 °C (O'Sullivan $et\ al.$, 2017). The T_{opt} derived from MMRT depends

332 on thermodynamic properties of contributing enzymes, particularly the $\Delta C_p^{\ddagger}$ value of the enzymes

333 involved in leaf respiration and this parameter was very tightly constrained across biomes. The T_{opt}

334 retrieved from MMRT represents the temperature where enzymes reached their theoretical maximum rate

335 of catalysis in the absence of other biochemical constraints. The measured T_{max}, also includes other

336 factors that can contribute to reduction in the overall rate of respiration, e.g., change in cell membrane

337 properties (Schrader $et\ al.$, 2004), respiration being uncoupled from mitochondrial electron transport

338 (Skulachev, 1998; Hüve $et\ al.$, 2011), or increased drought stress (Atkin & Macherel, 2009) at high

339 temperature. These factors lead to a 'burst' of R around 47°C (O'Sullivan $et\ al.$, 2013), that varies

340 between species and is presumably due to variation of other leaf traits, e.g., leaf size(Wright $et\ al.$, 2017),

341 than the enzymes involved in respiration. Hence, we hypothesize that the T_{opt} from MMRT and the

342 measured T_{max} describe the temperature response of R at level of the contributing metabolic enzymes and

343 at the whole leaf level, respectively. A higher T_{opt} than T_{max} suggests a higher thermal tolerance of

344 respiratory enzymes than the whole leaf. If this hypothesis is correct it argues that thermal response of

345 respiratory enzymes in leaves are highly conserved while leaves adapt to different climates by varying

346 leaf traits, such as leaf size, which demonstrates a clear consistent latitudinal gradient, e.g., large-leaved

14

347   species predominate in wet, hot, sunny environments (Wright *et al.*, 2017). This conserved temperature

348   response of plant leaf respiration across geophysical gradient or evolutionary scale is worth further

349   exploring. Nevertheless, MMRT provides a tool to explore the thermodynamic properties of respiratory

350   enzymes. The information could be useful to understand regulations of R under a warmer climate and

351   predict the short-term temperature response of R accurately.

352

358   **References**

359   Adams MA, Rennenberg H, Kruse J (2016) Different models provide equivalent predictive power for

360   cross-biome response of leaf respiration to temperature. *Proceedings of the National Academy of*

361   *Sciences of the United States of America*, **113**, E5993–E5995.

362   Alster CJ, Baas P, Wallenstein MD, Johnson NG, von Fischer JC (2016) Temperature Sensitivity as a

363   Microbial Trait Using Parameters from Macromolecular Rate Theory. *Frontiers in Microbiology*, **7**,

364   1821.

365   Arcus VL, Pudney CR (2015) Change in heat capacity accurately predicts vibrational coupling in enzyme

366   catalyzed reactions. *FEBS letters*, **589**, 2200–6.

367   Arcus VL, Prentice EJ, Hobbs JK et al. (2016) On the temperature dependence of enzyme-catalyzed rates.

368   *Biochemistry*, **55**, 1681–1688.

369   Atkin OK, Macherel D (2009) The crucial role of plant mitochondria in orchestrating drought tolerance.

370   *Annals of Botany*, **103**, 581–597.

371   Atkin OK, Tjoelker MG (2003) Thermal acclimation and the dynamic response of plant respiration to

372   temperature. *Trends in Plant Science*, **8**, 343–351.

373   Atkin OK, Bloomfield KJ, Reich PB et al. (2015) Global variability in leaf respiration in relation to

374   climate, plant functional types and leaf traits. *New Phytologist*, **206**, 614–636.

375   Buchanan CL, Connaris H, Danson MJ, Reeve CD, Hough DW (1999) An extremely thermostable

376   aldolase from Sulfolobus solfataricus with specificity for non-phosphorylated substrates. *The*

377   *Biochemical journal*, **343**, 563–70.

378   Buchanan BB, Gruissem W, Jones RL (2015) *Biochemistry & Molecular Biology of Plants*. John Wiley

379   & Sons, Ltd, West Sussex, UK, 634-635 pp.

380   Canadell JG, Le Quéré C, Raupach MR et al. (2007) Contributions to accelerating atmospheric CO2

381   growth from economic activity, carbon intensity, and efficiency of natural sinks. *Proceedings of the*

382   *National Academy of Sciences*, **104**, 18866–18870.

383   Ciais P, Sabine C, Bala G et al. (2013) *Carbon and Other Biogeochemical Cycles* (eds Stocker TF, Qin D,

384   Plattner G-K, Tignor M, Allen SK, J., Boschung, Nauels A, Xia Y, Bex V, P.M. Midgle).

385   Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press.

386   Daniel RM, Danson MJ (2010) A new understanding of how temperature affects the catalytic activity of

387   enzymes. *Trends in Biochemical Sciences*, **35**, 584–591.

388   Davidson EA, Janssens IA (2006) Temperature sensitivity of soil carbon decomposition and feedbacks to

389   climate change. *Nature*, **440**, 165–173.

390   Heskel MA, Atkin OK, O'Sullivan OS et al. (2016a) Reply to Adams et al.: Empirical versus process-

391   based approaches to modeling temperature responses of leaf respiration. *Proceedings of the National*

392   *Academy of Sciences*, **113**, E5996–E5997.

393   Heskel MA, O'Sullivan OS, Reich PB et al. (2016b) Convergence in the temperature response of leaf

394   respiration across biomes and plant functional types. *Proceedings of the National Academy of*

395   *Sciences*, **113**, 3832–3837.

396   Hobbs JK, Jiao W, Easter AD, Parker EJ, Schipper LA, Arcus VL (2013) Change in heat capacity for

397   enzyme catalysis determines temperature dependence of enzyme catalyzed rates. *ACS chemical*

398   *biology*, **8**, 2388–93.

399   Hüve K, Bichele I, Rasulov B, Niinemets Ü (2011) When it is too hot for photosynthesis: heat-induced

400   instability of photosynthesis in relation to respiratory burst, cell permeability changes and H2O2

401   formation. *Plant, Cell & Environment*, **34**, 113–126.

402   IPCC (2013) *Climate Change 2013: the physical science basis*. Cambridge, UK & New York, NY, USA:

403   Cambridge University Press.

404   Kruse J, Adams MA (2008) Three parameters comprehensively describe the temperature response of

405   respiratory oxygen reduction. *Plant, Cell & Environment*, **31**, 954–967.

406   Kruse J, Rennenberg H, Adams MA (2011) Steps towards a mechanistic understanding of respiratory

407   temperature responses. *New Phytologist*, **189**, 659–677.

408   Lloyd J, Taylor J (1994) On the temperature dependence of soil respiration. *Functional ecology*, **8**, 315–

409   323.

17

410 Ma S, Osuna JL, Verfaillie J, Baldocchi DD (2017) Photosynthetic responses to temperature across leaf–

411   canopy–ecosystem scales: a 15-year study in a Californian oak-grass savanna. *Photosynthesis*

412   *Research*, **132**, 277–291.

413 Noguchi K, Yamori W, Hikosaka K, Terashima I (2015) Homeostasis of the temperature sensitivity of

414   respiration over a range of growth temperatures indicated by a modified Arrhenius model. *New*

415   *Phytologist*, **207**, 34–42.

416 O'Sullivan OS, Weerasinghe KWLK, Evans JR, Egerton JJG, Tjoelker MG, Atkin OK (2013) High-

417   resolution temperature responses of leaf respiration in snow gum (Eucalyptus pauciflora) reveal

418   high-temperature limits to respiratory function. *Plant, cell & environment*, **36**, 1268–84.

419 O'Sullivan OS, Heskel MA, Reich PB et al. (2017) Thermal limits of leaf metabolism across biomes.

420   *Global Change Biology*, **23**, 209–223.

421 Ow LF, Griffin KL, Whitehead D, Walcroft AS, Turnbull MH (2008a) Thermal acclimation of leaf

422   respiration but not photosynthesis in Populus deltoides x nigra. *New Phytologist*, **178**, 123–134.

423 Ow LF, Whitehead D, Walcroft AS, Turnbull MH (2008b) Thermal acclimation of respiration but not

424   photosynthesis in Pinus radiata. *Functional Plant Biology*, **35**, 448–461.

425 Prentice I, Farquhar G, Fasham M et al. (2001) The carbon cycle and atmospheric carbon dioxide. In:

426   *Climate Change 2001: the scientific basis. Contribution of Working Group I to the third assessment*

427   *report of the Intergovernmental Panel on Climate Change* (eds Houghton J, Ding Y, Griggs D,

428   Noguer M, van der Linden P, Dai X, Maskell K, Johnson C), pp. 183–237. Cambridge, UK:

429   Cambridge University.

430 Robinson JM, O'Neill TA, Ryburn J, Liang LL, Arcus VL, Schipper LA (2017) Rapid laboratory

431   measurement of the temperature dependence of soil respiration and application to seasonal changes

432   in three diverse soils. *Biochemistry*, **133**, 101–112.

433 Schipper LA, Hobbs JK, Rutledge S, Arcus VL (2014) Thermodynamic theory explains the temperature

434   optima of soil microbial processes and high Q10 values at low temperatures. *Global change biology*,

435   **20**, 3578–86.

436   Schrader SM, Wise RR, Wacholtz WF, Ort DR, Sharkey TD (2004) Thylakoid membrane responses to

437   moderately high leaf temperature in Pima cotton. *Plant, Cell and Environment*, **27**, 725–735.

438   Skulachev VP (1998) Uncoupling: new approaches to an old problem of bioenergetics. *Biochimica et*

439   *Biophysica Acta (BBA) - Bioenergetics*, **1363**, 100–124.

440   Slot M, Kitajima K (2015) General patterns of acclimation of leaf respiration to elevated temperatures

441   across biomes and plant types. *Oecologia*, **177**, 885–900.

442   Taylor AE, Giguere AT, Zoebelein CM, Myrold DD, Bottomley PJ (2016) Modeling of soil nitrification

443   responses to temperature reveals thermodynamic differences between ammonia-oxidizing activity of

444   archaea and bacteria. *The ISME Journal*, **11**, 896–908.

445   Thomas TM, Scopes RK (1998) The effects of temperature on the kinetics and stability of mesophilic and

446   thermophilic 3-phosphoglycerate kinases. *The Biochemical journal*, **330**, 1087–95.

447   Tjoelker MG, Oleksyn J, Reich PB (2001) Modelling respiration of vegetation: evidence for a general

448   temperature-dependent Q10. *Global Change Biology*, **7**, 223–230.

449   Vanderwel MC, Slot M, Lichstein JW et al. (2015) Global convergence in leaf respiration from estimates

450   of thermal acclimation across time and space. *New Phytologist*, **207**, 1026–1037.

451   Wright IJ, Dong N, Maire V et al. (2017) Global climatic drivers of leaf size. *Science (New York, N.Y.)*,

452   **357**, 917–921.

453

454

455   **Table1** The mean values and standard errors of a(MMRT), $\Delta H_{T_0}^{\ddagger}$ and $\Delta C_P^{\ddagger}$, optimum temperature (T_{opt}) and

456   inflection temperature (T_{inf}) from MMRT across Biomes and PFTs

Biomes	a(MMRT)	$\Delta H_{T_0}^{\ddagger}$ (kJ mol^{-1})	$\Delta C_P^{\ddagger}$ (kJ mol^{-1} K^{-1})	T_{opt} (°C)	T_{inf} (°C)	N of fits (species/leaf)	N of T_{opt}/T_{inf} (species/leaf)
Tu	0.9194±0.1033[a]	52.3±1.2[a]	-1.3±0.1[a]	64.0±3.2[a]	38.4±2.0[a]	20/79	19/59
BF	0.0150±0.0819[cd]	50.2±1.3[a]	-0.4±0.2[a]	70.1±3.8[a]	42.6±2.3[a]	25/96	18/43
TeDF	0.2806±0.0995[de]	56.2±2.8[a]	0.02±0.3[a]	76.0±5.5[a]	48.3±3.5[a]	10/38	4/7
TeW	0.2931±0.0571[bc]	56.1±3.0[a]	-0.3±0.3[a]	64.2±2.2[a]	40.5±1.2[a]	67/193	40/81
TeRF	0.0107±0.1248[cd]	52.2±2.0[a]	-0.2±0.2[a]	79.5±4.8[a]	48.6±2.8[a]	12/45	7/12
TrRF_lw	-0.5440±0.0716[e]	53.6±1.3[a]	-0.3±0.1[a]	65.9±2.0[a]	40.9±1.2[a]	81/205	49/75
TrRF_hi	0.5252±0.0854[ab]	56.0±3.5[a]	-0.7±0.2[a]	70.7±4.5[a]	42.8±3.9[a]	16/17	10/10
PFTs							
C$_3$H	0.7453±0.1352[a]	52.3±1.2[a]	-1.4±0.2[a]	67.7±3.5[a]	40.1±2.3[a]	13/50	13/43
SEv	0.3130±0.1042[ab]	50.2±1.3[a]	-0.5±0.4[a]	61.3±2.6[a]	38.7±1.3[a]	35/104	24/47
NlEv	0.3745±0.1434[ab]	56.2±2.8[a]	-0.6±0.2[a]	72.6±3.9[a]	45.3±2.5[a]	13/48	8/19
BlDcTmp	-0.0460±0.0819[bc]	56.1±3.0[a]	-0.5±0.2[a]	67.7±3.0[a]	41.7±1.8[a]	40/150	28/66
BlEvTmp	0.2907±0.0828[bc]	52.2±2.0[a]	0.1±0.4[a]	70.9±4.3[a]	44.2±2.5[a]	34/104	16/28
BlEvTrp	-0.3523±0.0744[c]	53.6±1.3[a]	-0.4±0.1[a]	67.2±1.9[a]	41.4±1.3[a]	93/207	56/82
BlDcTrp	-0.3299±0.2802[bc]	56.0±3.5[a]	-0.7±0.5[a]	59.8±10.0[a]	39.5±2.9[a]	3/10	2/2
Global Mean	-0.0008±0.0460	54.0±1.0	-0.4±0.1	67.0±1.2	41.4±0.7		

457

458   Tu: Tundra, BE: Boreal Forest, TeDF: Temperature Deciduous Forest, TeW: Temperature Woodland,

459   TeRF: Temperature Rainforest, TrRF_lw: Tropical Rainforest at low elevation, TrRF_hi: Tropical

460   Rainforest at high elevation. C$_3$H: C3 Herbaceous, SEv: Evergreen Shrubs, NIEv: Needle-leaf evergreen,

461   BlDcTmp: Broadleaf Deciduous Temperate, BlEvTmp: Broadleaf Evergreen Temperate, BlEvTrp:

462   Broadleaf Evergreen Tropical, BlDcTrp: Broadleaf Deciduous Tropical

463   Within columns, values with the same letter were not significantly different for the pairwise comparison

464   across Biomes and PFTs. N of fits (species/leaf) is the initial sample size of the data for fitting MMRT,

465   species/leaf denotes the number of species or leaf samples in each biome and PFT. N of T_{opt}/T_{inf} denotes

466   the number of credible fits in calculating the T_{opt} and T_{inf} within biological meaningful range.

467

468   **Fig. 1** The correspondence between MMRT and LP function in describing the temperature response of

469   leaf respiration. The black and grey squares are the predicted optimum temperature (T_{opt}) from MMRT

470   (62.32 °C) and LP (62.07 °C) functions respectively. The black and grey circles are the inflection

471   temperature (T_{inf}), 34.40 and 37.25°C from MMRT and LP, respectively. T_{opt} and T_{inf} in MMRT and LP

472   are mainly defined by the curvature terms from MMRT and LP, i.e., $\Delta C_P^{\ddagger}$ and c, respectively. The T_{opt}

473   and T_{inf} could varies between 25 and 100 °C depending on the magnitude of negative curvature terms.

474

475   **Fig. 2** Comparisons of predictive power of MMRT, LP (Log-Polynomial) and Arrhenius models,

476   showing both MMRT and LP models are equivalent and more powerful than the Arrhenius model in

477   characterizing the temperature response of R. (a) shows the capability of three models in characterising

478   the temperature response of measured leaf respiration using the R-T curve of species *Anemone*

479   *narcissiflora* in tundra (b) shows the corresponding residuals from MMRT (solid circles), LP (open

480   circles line) and Arrhenius (open squares) models from panel (a). (c) compares AICc values across the

481   three models.

482

483   **Fig. 3** Comparisons between fitted parameters derived from MMRT and polynomial following Eq.7. All

484   the parameters between polynomial and MMRT are very tightly correlated.

485

486   **Fig. 4** (a) The relationship between a(MMRT) and aridity index (the ratio between mean annual

487   precipitation (MAP) and potential evapotranspiration (PET)) across 18 sites covering different climates.

488   The black dash line is a linear regression fit ($y=-0.64x+ 0.59$). The colour demonstrates the mean annual

489   temperature (MAT) for each of the sites and the symbol size increases with the mean annual precipitation

490   (MAP). (b) shows the temperature response curve from MMRT at two sites with contrasting environments.

491   The solid line indicates the temperature response of leaf respiration at Toolik, Alaska, US using the mean

492   parameters of MMRT retrieved from 79 individual lnR-T curves. The dash line represents the mean

493   temperature response of plant leaves at Canberra, Australia using the retrieved parameters from 15

494   individual lnR-T curves. The vertical dish line indicates the reference temperature, T_0 (298.15K, 25°C).

495   The grey bands show the R between MAT and mean temperature in the warmest quarter (TWQ) of the year.

496   The similar magnitude of R from two sites suggests a homeostasis of respiration in plants that maintains a

497   comparable R under the growth temperature of their habitats.

498

(a) x-axis: a; y-axis: $\ln \dfrac{k_B T_0}{h} - \dfrac{\Delta G^{\ddagger}_{T_0}}{RT_0}$

(b) x-axis: b; y-axis: $\dfrac{1}{T_0} + \dfrac{\Delta H^{\ddagger}_{T_0}}{RT_0^2}$

(c) x-axis: c; y-axis: $\dfrac{\Delta C^{\ddagger}_P}{2RT_0^2}$

(a) $R^2=0.65$, n=18, $p<0.0001$

MAP(mm): 225 → 4045

MAT(°C)

(b)
- Toolik, Alaska, US
- Canberra, Australia
- R between MAT and TWQ

$T_0 = 25^oC$, $a(MMRT) = 2.5 \mu mol CO_2\, m^{-2} s^{-1}$

$a(MMRT) = 0.5 \mu mol CO_2\, m^{-2} s^{-1}$