

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

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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  $\text{CO}_2$  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  $67.0 \pm 1.2$  °C and the  
39 maximum temperature sensitivity at  $41.4 \pm 0.7$  °C from MMRT. The average curvature (average  
40 negative  $\Delta C_p^\ddagger$ ) was  $-1.2 \pm 0.1$   $\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . 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.

## 47 **Introduction**

48 Leaf respiration ( $R$ ) contributes  $c.30$  Pg (30 billion metric tons) carbon per year to the atmosphere  
49 (Prentice *et al.*, 2001; Canadell *et al.*, 2007; IPCC, 2013), about 4 times higher than the industrial CO<sub>2</sub>  
50 emissions ( $\sim 8$  Pg C yr<sup>-1</sup>) between 2002 to 2011 (IPCC the fifth assessment report Table 6.1, chapter 6  
51 (Ciais *et al.*, 2013)). Consequently, small changes in  $R$  have the potential to make a huge impact on the  
52 atmospheric CO<sub>2</sub> concentrations. It is generally predicted that  $R$  will increase with the increasing mean  
53 global temperature from the current earth system model projections. Increases in  $R$  are not linear with  
54 temperature but rather exponential as modelled by the Arrhenius equation. However, departures from  
55 Arrhenius behaviour are well known for many biologically driven reactions such as leaf respiration,  
56 photosynthesis and soil carbon decomposition (Lloyd & Taylor, 1994; Tjoelker *et al.*, 2001; Alster *et al.*,  
57 2016; Ma *et al.*, 2017; Robinson *et al.*, 2017).

58 In a recent study, Heskell *et al.* (2016b) reported a universal convergence in temperature response of  $R$   
59 across different biomes and plant functional types (PFTs) using a global dataset of plant leaf respiration  
60 measurements. They demonstrated a consistent curvature in log-transformed  $R$  vs temperature plots that  
61 was best fit using a second-order log-polynomial model (LP model) for a large number of  $R$  versus  
62 temperature datasets. They compared the LP model to four other conventional models (exponential fixed-  
63 Q<sub>10</sub>, Arrhenius, Lloyd & Taylor and variable-Q<sub>10</sub>) and showed improved predictive power in estimating  
64 the carbon release from vegetation. An modified Arrhenius model with 3 components, which describes  
65 the temperature dependence of activation energy in Arrhenius model as a second-order polynomial  
66 function, also provides equivalent fits as the LP model (Kruse & Adams, 2008; Kruse *et al.*, 2011; Adams  
67 *et al.*, 2016; Heskell *et al.*, 2016a). Since respiratory metabolism in a leaf involves a series of enzyme-  
68 catalyzed reactions, via the tricarboxylic acid (TCA) cycle or cytochrome pathways (Buchanan *et al.*,  
69 2015), a mechanistic underpinning of the temperature response of  $R$  may be found in the temperature  
70 dependence of enzyme-catalyzed reaction rates.

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

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 Heskell *et al.* (2016b). Indeed, we show that the two models  
82 are nearly equivalent mathematically. Specifically, we use the large  $R$  dataset collected by Heskell 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 Heskell *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<sub>2</sub> exchange between leaf  
93 and atmosphere are provided in Heskell *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).

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:

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

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

109 where  $\kappa$ ,  $k_B$ ,  $h$  and  $R$  refer to the transmission coefficient (here,  $\kappa$  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:

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

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 Heskell 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 Heskell *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).

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

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):

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

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 Heskell and colleagues, we will call this  $a(\text{MMRT})$ . 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 Heskell *et al.* (2016b) can be  
 158 rewritten as:

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

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

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

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  $\sim 10$  °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,  $\Delta H_{T_0}^\ddagger$ ,  $\Delta S_{T_0}^\ddagger$  and  $\Delta C_P^\ddagger$ ; 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  $\ln R$ -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.,  $\Delta H_{T_0}^\ddagger$ ,  $\Delta S_{T_0}^\ddagger$  and  $\Delta C_P^\ddagger$ , 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),  $\Delta H_{T_0}^\ddagger$ ,  $\Delta C_P^\ddagger$ ,  $T_{opt}$  and  $T_{inf}$  were statistically compared across 7 biomes and 7 plant functional  
193 types (PFTs) using mixed effect model as Heskell *et al.* (2016b). The Tukey's honestly significant  
194 difference (HSD) test was used to conduct the *post hoc* intra-group comparisons.

## 195 **Results**

### 196 *Comparisons between fits using Arrhenius, MMRT and LP equations*

197 All three models, Arrhenius (Eq.1), MMRT (Eq.3) and LP (Eq.6) were able to describe the temperature  
198 response of  $R$  (Fig. 2a), although it is clear from the residuals that the MMRT and LP models outperform  
199 the Arrhenius function (Fig. 2b). ANOVA of AICc among 3 models also showed that both MMRT and  
200 LP models were consistently better than the Arrhenius model in predicting the temperature response of  $R$   
201 across 673 individual  $\ln R$ - $T$  curves, with statistically significant lower AICc ( $p < 0.0001$ ) values from both  
202 MMRT and LP models compared to the Arrhenius function (Fig. 2c). This conclusion is consistent with  
203 the results of Heskell *et al.* (2016b), who demonstrated that the LP model better characterized the  
204 temperature response of  $R$  when compared to four other Arrhenius-based models. MMRT provided  
205 equivalent predictive power for the temperature response of  $R$  when compared to the empirical LP model  
206 since there was no statistical difference among AICc values ( $p = 0.99$ ) between MMRT and LP models.  
207 This is unsurprising given the near equivalence of the mathematical functions for the MMRT and LP  
208 models or a modified Arrhenius model proposed by Adams *et al.* (2016).

### 209 *Bridging MMRT and polynomial models*

210 The parameters derived from fits between the LP and MMRT models are nearly identical (Fig. 3). The  $R$   
211 value at  $T_0$  (298.15K, 25°C), i.e., parameter  $a$  in the LP model, is almost the same as that calculated from  
212 MMRT at  $T_0$  (Fig. 3a), with an inconsequential difference between  $a$  and  $R$  at  $T_0$  ( $a - R_{25}$ ) of  $-0.0011 \mu\text{mol}$   
213  $\text{CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ . Parameter  $b$  in the LP model, is commensurate with that from MMRT (Fig. 3b), with a  
214 difference of  $9.1 \times 10^{-5} \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1} \text{ K}^{-1}$ . The curvature term between MMRT and LP is also equivalent  
215 (Fig. 3c). The difference between  $c$  and  $\Delta C_p^* / 2RT_0^2$  is  $-2.2 \times 10^{-4} \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1} \text{ K}^{-2}$ , which is equivalent  
216 to a difference of  $-0.3 \text{ kJ mol}^{-1} \text{ K}^{-1}$  in  $\Delta C_p^*$ . Thus, MMRT and LP functions both model  $R$  equally (Fig. 1)  
217 and provide closely comparable parameters, suggesting that we can either use MMRT or the LP function  
218 to characterize the temperature response of  $R$ .

### 219 *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 Heskell *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 Heskell *et al.* (2016b),  $0.1012 \mu\text{mol m}^{-2} \text{s}^{-1} \text{C}^{-1}$  and  $-0.0005 \mu\text{mol m}^{-2}$   
 232  $\text{s}^{-1} \text{C}^{-2}$ , are equivalent to  $\Delta H_{T_0}^\ddagger = 53.8 \text{ kJ mol}^{-1}$  and  $\Delta C_p^\ddagger = -0.7 \text{ kJ mol}^{-1} \text{K}^{-1}$  in MMRT, respectively. The  
 233 results from MMRT agree with the convergent temperature response of  $R$  in Heskell *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  $R$   $67.0 \text{ }^\circ\text{C}$  and  $41.4 \text{ }^\circ\text{C}$ , 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 ( $C_3H$ ) 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 Heskell and colleagues (Heskell *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 Heskell *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

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 ( $\Delta C_p^\ddagger = -1.2 \pm 0.1 \text{ kJ.mol}^{-1}\text{K}^{-1}$ ) for plant respiration is significantly less than the average  
274 curvature seen for heterotrophic soil respiration accurately measured in the laboratory ( $\Delta C_p^\ddagger = -2.1 \pm 0.1$   
275  $\text{kJ.mol}^{-1}\text{K}^{-1}$ )(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 Heskell *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  $-1.2 \pm 0.1 \text{ kJ.mol}^{-1}\text{K}^{-1}$  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). Heskell *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 (Table 1) 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  $R$  (Heskell *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  $a(\text{MMRT})$  from cool/dry to high temperature/humid environment (Fig. 4b). The  
313 pattern of  $a(\text{MMRT})$  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  $a(\text{MMRT})$  than MAT, suggesting a higher  $a(\text{MMRT})$  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  $a(\text{MMRT})$ ). 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 (Table 1). 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

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

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356 available at <https://waiber.com/>. Please contact Liyin L. Liang ([lssllyin@gmail.com](mailto:lssllyin@gmail.com)), Vickery L. Arcus  
357 ([varcus@waikato.ac.nz](mailto:varcus@waikato.ac.nz)) and Louis A. Schipper ([schipper@waikato.ac.nz](mailto:schipper@waikato.ac.nz)) for further information.

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453

454

455 **Table1** The mean values and standard errors of  $a(\text{MMRT})$ ,  $\Delta H_{T_0}^{\ddagger}$  and  $\Delta C_p^{\ddagger}$ , optimum temperature ( $T_{\text{opt}}$ ) and  
 456 inflection temperature ( $T_{\text{inf}}$ ) from MMRT across Biomes and PFTs

Biomes	$a(\text{MMRT})$	$\Delta H_{T_0}^{\ddagger}$ (kJ mol <sup>-1</sup> )	$\Delta C_p^{\ddagger}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$T_{\text{opt}}$ (°C)	$T_{\text{inf}}$ (°C)	N of fits (species/leaf)	N of $T_{\text{opt}}/T_{\text{inf}}$ (species/leaf)
Tu	0.9194±0.1033 <sup>a</sup>	52.3±1.2 <sup>a</sup>	-1.3±0.1 <sup>a</sup>	64.0±3.2 <sup>a</sup>	38.4±2.0 <sup>a</sup>	20/79	19/59
BF	0.0150±0.0819 <sup>cd</sup>	50.2±1.3 <sup>a</sup>	-0.4±0.2 <sup>a</sup>	70.1±3.8 <sup>a</sup>	42.6±2.3 <sup>a</sup>	25/96	18/43
TeDF	0.2806±0.0995 <sup>de</sup>	56.2±2.8 <sup>a</sup>	0.02±0.3 <sup>a</sup>	76.0±5.5 <sup>a</sup>	48.3±3.5 <sup>a</sup>	10/38	4/7
TeW	0.2931±0.0571 <sup>bc</sup>	56.1±3.0 <sup>a</sup>	-0.3±0.3 <sup>a</sup>	64.2±2.2 <sup>a</sup>	40.5±1.2 <sup>a</sup>	67/193	40/81
TeRF	0.0107±0.1248 <sup>cd</sup>	52.2±2.0 <sup>a</sup>	-0.2±0.2 <sup>a</sup>	79.5±4.8 <sup>a</sup>	48.6±2.8 <sup>a</sup>	12/45	7/12
TrRF_lw	-0.5440±0.0716 <sup>e</sup>	53.6±1.3 <sup>a</sup>	-0.3±0.1 <sup>a</sup>	65.9±2.0 <sup>a</sup>	40.9±1.2 <sup>a</sup>	81/205	49/75
TrRF_hi	0.5252±0.0854 <sup>ab</sup>	56.0±3.5 <sup>a</sup>	-0.7±0.2 <sup>a</sup>	70.7±4.5 <sup>a</sup>	42.8±3.9 <sup>a</sup>	16/17	10/10
PFTs							
C <sub>3</sub> H	0.7453±0.1352 <sup>a</sup>	52.3±1.2 <sup>a</sup>	-1.4±0.2 <sup>a</sup>	67.7±3.5 <sup>a</sup>	40.1±2.3 <sup>a</sup>	13/50	13/43
SEv	0.3130±0.1042 <sup>ab</sup>	50.2±1.3 <sup>a</sup>	-0.5±0.4 <sup>a</sup>	61.3±2.6 <sup>a</sup>	38.7±1.3 <sup>a</sup>	35/104	24/47
NIEv	0.3745±0.1434 <sup>ab</sup>	56.2±2.8 <sup>a</sup>	-0.6±0.2 <sup>a</sup>	72.6±3.9 <sup>a</sup>	45.3±2.5 <sup>a</sup>	13/48	8/19
BLDcTmp	-0.0460±0.0819 <sup>bc</sup>	56.1±3.0 <sup>a</sup>	-0.5±0.2 <sup>a</sup>	67.7±3.0 <sup>a</sup>	41.7±1.8 <sup>a</sup>	40/150	28/66
BLIEvTmp	0.2907±0.0828 <sup>bc</sup>	52.2±2.0 <sup>a</sup>	0.1±0.4 <sup>a</sup>	70.9±4.3 <sup>a</sup>	44.2±2.5 <sup>a</sup>	34/104	16/28
BLIEvTrp	-0.3523±0.0744 <sup>c</sup>	53.6±1.3 <sup>a</sup>	-0.4±0.1 <sup>a</sup>	67.2±1.9 <sup>a</sup>	41.4±1.3 <sup>a</sup>	93/207	56/82
BLDcTrp	-0.3299±0.2802 <sup>bc</sup>	56.0±3.5 <sup>a</sup>	-0.7±0.5 <sup>a</sup>	59.8±10.0 <sup>a</sup>	39.5±2.9 <sup>a</sup>	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<sub>3</sub>H: C3 Herbaceous, SEv: Evergreen Shrubs, NIEv: Needle-leaf evergreen,  
 461 BLDcTmp: Broadleaf Deciduous Temperate, BLIEvTmp: Broadleaf Evergreen Temperate, BLIEvTrp:  
 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  $T_{\text{opt}}/T_{\text{inf}}$  denotes  
 466 the number of credible fits in calculating the  $T_{\text{opt}}$  and  $T_{\text{inf}}$  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  $\ln R$ -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  $\ln R$ - $T$  curves. The vertical dashed 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







