



Reconciling different equations for proton conduction using the Meyer-Neldel compensation rule

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[1] Proton conduction in nominally anhydrous minerals is the likely explanation for moderate values of electrical resistivity observed in the lithospheric and sublithospheric mantle. However, results from the various laboratories making the controlled measurements on mantle minerals, predominantly olivine, are not in agreement with one another. Importantly, the groups use different formalisms to fit their experimental data. In this paper, we show that neither of the two formalisms employed by the various laboratories is consistent with the Meyer-Neldel Rule (MNR), or Compensation Law, by which the preexponent term of the Arrhenian equation is linearly related to the activation energy term. We also demonstrate why the formalism of Karato and colleagues can be used at low water contents (100 wt ppm and below), whereas at higher water contents (above 300 wt ppm), the formalism of Yoshino's and Poe's labs needs to be employed. A new MNR self-consistent formalism is presented that is applicable over all water contents. MNR consistency appears to operate for most processes that can be described by an Arrhenius equation, so its adoption through an MNR consistent formalism is highly recommended when fitting experimental observations.

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1. Introduction

[2] The Arrhenius equation is a mathematical description of any thermally activated process giving a value of a parameter, $X(T)$, at a given temperature T , and is

$$X(T) = X_0 \exp(-E/kT), \quad (1)$$

where X_0 is the preexponent term, E is the activation energy of the process (in Joules), k is the

Boltzmann's constant (in Joules/Kelvin), and T is the temperature (in Kelvin). It was initially proposed in 1884 by Dutch physical chemist Jacobus Henricus van't Hoff to describe the temperature dependence of chemical reaction rates. Five years later Swedish physicist-chemist Svante August Arrhenius, working with van't Hoff in Amsterdam after spending time with Ludwig Boltzmann in Graz, provided a theoretical justification for it based on his work on the disassociation of electrolytes [Arrhenius, 1889]. Equation (1) is as remarkably

successful as it is simple, and finds application in many areas of science besides the obvious ones on reaction rates [e.g., *Hanggi et al.*, 1990], ranging from soil respiration [*Lloyd and Taylor*, 1994] to the growth rate of bacterial cultures [*Ratkowsky et al.*, 1982] to the drying of thin slices of garlic [*Madamba et al.*, 1996].

[3] Initially in chemistry in the middle to late 1920s [*Constable*, 1925; *Cremer and Schwab*, 1929; *Schwab*, 1929; *Polissar*, 1930, 1932], then independently later in physics in the mid-1930s [*Meyer and Neldel*, 1937], scientists began to observe empirically a linear relationship between the natural logarithm of the preexponent term X_0 and the activation energy E (more correctly activation enthalpy) for any process that could be described by an Arrhenius equation. A simple linear relation was found to hold for many materials and processes,

$$\ln(X_0) = a + bE \quad (2)$$

where intercept a and slope b are constants. This formula, termed the Meyer-Neldel rule (MNR) [*Meyer and Neldel*, 1937] in physics and the Compensation Law, Compensation Effect, Cremer-Constable relation, or the isokinetic relationship in chemistry [*Linert and Yelon*, 2013], also in different guises termed the Barclay-Butler rule [*Barclay and Butler*, 1938], the θ rule [*Schwab*, 1950], the Smith-Topley effect [*Manche and Carroll*, 1979], and the Zawadzki-Bretsznajder rule [*Zawadzki and Bretsznajder*, 1935], is upheld in many areas of materials science in physics, chemistry, and biology, including compounds in semiconductors, various reduced oxide semiconductors, biological death rates, and chemical reactions [see *Yelon et al.*, 1992, and references therein; also special recent volume of *Monatsh. Chem.*, 144(1–2), edited by *Linert and Yelon*, 2013].

[4] Substituting equation (2) into equation (1) yields an expression for X that does not use the preexponent term X_0 , viz.,

$$\begin{aligned} X &= X_0 \exp(-E/kT), \\ &= \exp(a + bE) \exp(-E/kT), \\ &= \exp(a) \exp((bkT - 1)E/kT). \end{aligned} \quad (3)$$

[5] Solid state physicists have examined and attempted to explain the existence of the MNR phenomenon for many years, advancing a number of speculative models [e.g., *Dyre*, 1986; *Stallinga*

and *Gomes*, 2005; *Banik*, 2009]. The explanation that appears to be currently most in favor is that it is a consequence of a one phonon activated process [*Yelon et al.*, 1992; *Boisvert et al.*, 1995; *Yelon et al.*, 2006; *Shimakawa and Aniya*, 2013]. The MNR is not without contention, even to the point of recent-renewal of the long-standing discussion on statistical significance of data fitting [*Exner*, 1964; *Barrie*, 2012b, 2012a, 2012c; *Yelon et al.*, 2012], and there does appear to be some exceptions [e.g., *Nowick et al.*, 1988]. However, more and more papers are being published that demonstrate its validity for a wide variety of Arrhenian processes, and the criticism that the MNR is contentious cannot be used as justification for ignoring this vast body of evidence and does a disservice to the sciences. Just because a theory has yet to have an established explanation does not mean that it can be willfully ignored. We geoscientists should be very aware of this, given the tortuous history of acceptance of plate tectonics since Wegner's theories were first published and ridiculed in the early part of the last century, and the problems encountered by geologists in the second half of the 19th century convincing the world that the rock record spoke of billions of years of tectonics countered by the age of the Earth estimations of Lord Kelvin, of between 20 Myr and 40 Myr, based on conductive cooling arguments made in ignorance of radioactive decay heating.

[6] Proton conduction observations in perovskite-structured KTaO_3 [*Scherban and Nowick*, 1992] and in LaNbO_4 [*Solis and Serra*, 2011] demonstrated that the MNR is obeyed for those materials. The latter showed that there were two MNRs operating, i.e., two different sets of MNR intercepts and gradients [a , b] that fit the observations; one set at high temperatures (above 550°C) in a tetragonal crystal structure with low activation energy (<0.75 eV), and another set at low temperatures (below 550°C) in a monoclinic crystal structure with high activation energy (>0.75 eV). The latter has an MNR intercept and gradient of -11.6 and 16.7 , respectively, whereas the former has values of -4.75 and 7.0 (intercepts modified from Figure 11 in *Solis and Serra* [2011] to convert from Ωcm to Ωm). Note that the MNR intercept and gradient for high temperature proton conduction is the same as that observed for polaron conduction in olivine (equation (4), see below). This observation, of higher activation energy of protons in the low temperature monoclinic fergusonite structure than in the high temperature scheelite structure, may explain the exceptions to the MNR previously

described by *Nowick et al.* [1988]. These observations lend substantial support to the conjecture that the MNR should be obeyed for proton conduction in olivine, and that the formalism to fit the laboratory measurements should be appropriately constructed to be MNR consistent.

[7] This empirically observed, almost always upheld rule can be employed to provide fundamental constraints on the derivation and estimation of X_0 and E from experimental data. Particularly, given their interrelationship defined by equation (2), if one has knowledge of MNR intercept a and slope b for the process under consideration, then the compatibility of estimates of X_0 and E from data fitting exercises can be tested.

[8] In the geosciences, there are many processes that are described by an Arrhenian relationship, such as polaron, electron, and proton conduction in rocks [see *Jones et al.*, 2012, and papers cited therein], diffusion of many species [*Zhao and Zheng*, 2007], and the viscosity of melts [e.g., *Baker and Vaillancourt*, 1995]. However, knowledge and appreciation of the MNR in the geosciences is low to absent, and the benefits, consequences, and limitations of applying the MNR have not been fully utilized. Exceptions to this are the recent papers by *Wu and Zheng* [2005] and *Zhang et al.* [2011].

[9] Many studies of electrical conduction and semiconduction in various materials demonstrate the validity of the MNR [see recent review by *Mehta*, 2010]. For Earth materials, in their compilation of laboratory measurements of conductivity of olivine, *Wu and Zheng* [2005] showed an astonishing plot between the natural logarithm of the preexponent ($\ln(\sigma_0)$, where σ_0 is in S/m) and the excitation enthalpy (E , in eV) with a very high correlation coefficient of 0.996 and a linear relationship of

$$\ln(\sigma_0) = -4.94 (\pm 0.34) + 6.68 (\pm 0.012)E \text{ (eV)}, \quad (4)$$

thus providing yet further substantiation of the validity of MNR when applied to conduction in silicate minerals. Note that these MNR intercept and gradient values are, astonishingly, very close to those observed by *Solis and Serra* [2011] (-4.75 and 7.00 , respectively) for proton conduction in tetragonal crystal structure (see above).

[10] The MNR provides a tool to test the compatibility and consistency of the derived preexponent and activation energy parameters, or of the validity of the parameterization itself as is examined here.

A pertinent example is the study of the electrical conductivity of olivine by *Constable et al.* [1992], who noted a linear relationship between the logarithm of the preexponential term (σ_0) and the activation energy (E). This linear relationship is inherent in the Arrhenian process as a consequence of the phenomenon encapsulated by the MNR, whereas *Constable et al.* [1992] considered it an experimental data fitting error. Those authors forced their experimental data to fit a preferred activation energy ($E = 1.6$ eV) and derived varying preexponent terms. This approach violates the MNR, as different σ_0 values will necessarily require different E values to be MNR consistent.

[11] In this paper, we focus on proton conduction in olivine and will show that neither of the two main formalisms used to fit the observations by the four laboratories making the requisite observations obey the Meyer-Neldel rule. We will further demonstrate why it is that two of the laboratories can use one particular formalism apparently successfully, whereas the other two laboratories can use a different one, also apparently successfully. The disparity is entirely due to the range of water contents explored by the laboratories. We will suggest an alternative formalism that is consistent with the Meyer-Neldel rule and is valid over all water contents. It is not the purpose of this paper to fit the disparate experimental data, especially given the contentions between the laboratories and the contradictions between their experimental observations, but to expose and promote the use of the MNR to the laboratory community and to outline an approach for defining the formalism appropriate for fitting the data that is MNR consistent.

2. Proton Conduction in Olivine

[12] Quantifying the amount and distribution of water in the mantle and its partitioning between the mantle minerals is key for furthering our understanding of the geodynamic processes that govern our planet, as the presence of water dramatically affects rheology and induces low temperature partial melting. As described in the recent review by *Pommier* [2014], water is involved in slab subduction, induced melting of the mantle wedge, and the genesis of flood basalts and komatiites. Conductivity studies offer the best way of obtaining information about water in the mantle [*Karato*, 2006], but for them to be useful key laboratory measurements have to be made, verified and substantiated.

[13] There are four laboratories world-wide making experimental observations of proton conduction in minerals (Karato's lab in the USA, Yoshino's lab in Japan, Poe's lab in Italy, and Wang's lab in China), and their data are fit to an Arrhenius model that is generally described by a preexponent term ($\sigma_{0p}C_w^r$) and an activation enthalpy term ($\Delta H_w - \alpha C_w^{1/3}$), both of which are functions of water content C_w , viz.,

$$\sigma_p(C_w, T) = \sigma_{0p} C_w^r \exp\left(\frac{-(\Delta H_w - \alpha C_w^{1/3})}{kT}\right) \quad (5)$$

where σ_p and σ_{0p} are conductivities (in S/m), C_w is water content (in wt%), ΔH_w is activation energy (in J), k is Boltzmann's constant (in J/K), T is absolute temperature (K), and r and α are dimensionless parameters. Karato's and Wang's [Huang *et al.*, 2005; Wang *et al.*, 2006, 2008; Dai and Karato, 2009; Karato, 2013] labs and others [Yang *et al.*, 2011, 2012] use a nonunity value of r and a zero value for α , whereas the labs of Yoshino [Yoshino *et al.*, 2009; Yoshino and Katsura, 2012] and Poe [Manthilake *et al.*, 2009; Poe *et al.*, 2010] set r to unity and determine a nonzero positive value for α . (Note that Wang's formalism also includes an iron dependent term and a pressure term that are ignored here as the effects of both are minor compared to the water content effect.)

[14] The exponent r on the preexponent water content C_w in Karato's and Wang's formalism is an

attempt to describe the nonlinear effects due to multiple hydrogen atoms in a single defect, but is ignored by Yoshino and Poe. We note that plastic deformation of olivine due to water content also includes an exponent term r on the water content for both diffusion and dislocation creep [Mei and Kohlstedt, 2000a, 2000b; Chu and Korenaga, 2012].

[15] In contrast, the coefficient α used by Yoshino and Poe is an attempt to describe activation energy dependence as a function of water content that results from more closely spaced defects, but is ignored by Karato and Wang. Water content C_w in this activation enthalpy term is taken to the power 1/3 following the standard solid-state physics equation for an n -type semiconductor [Yoshino and Katsura, 2013].

[16] The laboratories have been robustly debating in the literature the merits of their own approaches and the failings of the others regarding basic experimental design, measurement methods, samples, sample techniques, etc. [Karato and Dai, 2009; Yoshino and Katsura, 2009; Yoshino, 2010; Karato, 2011; Yang, 2012; Karato and Wang, 2013; Yoshino and Katsura, 2013], and to date no clear consensus has emerged. Most recently, F. Gaillard (personal communication, 2013) and Karato and Dai [2013] pointed out the inconsistency in the water contents listed in Table 1 of Yoshino *et al.* [2009] with the water contents in H/10⁶ Si being 10 times lower than the water contents listed

Table 1. Parameters for the Proton Conduction Terms in Equation (5) for Hydrogen Diffusion Water Models for Olivine From the Three Laboratories Plus the Field-Based Estimates of Jones *et al.* [2012]^a

Reference	$\log_{10}(\sigma_{0p})$	r	ΔH_w (eV)	α	Comments
Huang <i>et al.</i> [2005]	2.56 +0.18, -0.15	0.66 ± 0.05	0.91 ± 0.03	0	Wadsleyite
	3.61 ± 0.10	0.69 ± 0.03	1.08 ± 0.02	0	Ringwoodite
Wang <i>et al.</i> [2006]	3.00 ± 0.4	0.62 ± 0.15	0.87 ± 0.05	0	
Wang <i>et al.</i> [2008] ^b	5.20 ± 0.4	0.67 ± 0.07	1.89 ± 0.09	0	Conducted at temperatures of 1000–1200°C
Yoshino <i>et al.</i> [2008]	2.60 +0.25, -0.66	<i>1</i>	1.49 ± 0.10	0.02 ± 0.02	Wadsleyite
	2.92 +0.19, -0.32	<i>1</i>	1.36 ± 0.05	0.16 ± 0.02	Ringwoodite
Dai and Karato [2009]	2.50 ± 0.5	0.72 ± 0.08	0.91 ± 0.10	0	Wadsleyite
Romano <i>et al.</i> [2009]	1.93	1.44	0.66	0	Wadsleyite
Yoshino <i>et al.</i> [2009]	1.90 ± 0.44	<i>1</i>	0.92 ± 0.04	0.16 ± 0.02	
Poe <i>et al.</i> [2010] ^c	2.59 ± 0.16	<i>1</i>	1.26 ± 0.04	1.18 ± 0.04	[1 0 0] axis
	3.46 ± 0.09	<i>1</i>	1.50 ± 0.05	1.43 ± 0.11	[0 1 0] axis
	1.02 ± 0.09	<i>1</i>	0.812 ± 0.016	0.70 ± 0.015	[0 0 1] axis
Fullea <i>et al.</i> [2011]	2.35 ± 0.11	<i>1</i>	1.19 ± 0.035	1.10 ± 0.055	Arithmetic averages of Poe <i>et al.</i> 's results
Yang [2012] ^c	0.93 ± 0.26	<i>1</i>	0.99 ± 0.042	0	[1 0 0] axis, 40 wt ppm
	0.93 ± 0.52	<i>1</i>	0.99 ± 0.076	0	[0 1 0] axis, 40 wt ppm
	0.38 ± 0.47	<i>1</i>	0.88 ± 0.065	0	[0 0 1] axis, 40 wt ppm
Jones <i>et al.</i> [2012]	3.05 ± 0.16	0.86 ± 0.08	0.91 ± 0.03	0.09 ± 0.08	Fit to observational data

^aItalicized values are implicit.

^bAlso includes an Arrhenius term due to Fe content: $\exp(\alpha X_{Fe}/RT)$, where $\alpha = 79 \pm 3$ kJ/mol, X_{Fe} is the iron fraction (100-Mg#/100), and R is the gas constant. Converting to $\exp(\alpha X_{Fe}/kT)$ for consistency gives $\alpha = 0.82 \pm 0.03$ eV (divide by 96.4869 to convert from kJ/mol to eV).

^cMeasurements made along the three crystallographic axes.

in wt%, and showed that the lower water contents yield conductivity values that are in reasonable agreement with Karato's lab. T. Yoshino (personal communication, 2013) is emphatic that the water contents in wt% are the correct ones, and that the disagreement persists. What has not received much attention is the validity of the two different formalisms used—this is the focus of this paper.

[17] This controversy and disagreement has the unfortunate and unsatisfactory consequence that those who wish to make use of the results of the effects of water on mantle minerals must make a decision as to which laboratory's values to choose over the others. For example, *Kelbert et al.* [2009] and *Khan et al.* [2011] choose Yoshino's parameters, whereas *Fullea et al.* [2011] and *Khan and Shankland* [2012] compare models derived using Karato's parameters against those using Yoshino's, and *Naif et al.* [2013] use Poe's.

[18] Of greatest concern is that in some instances conclusions drawn about the state of the Earth using one set of parameters are invalidated when using the other set—not that we are certain which is correct. For example, the assertion by *Yoshino et al.* [2006] that hydrous olivine is unable to account for the conductivity anomaly at the top of the asthenosphere is contradicted by *Wang et al.* [2006] in the very same issue of *Nature* [see News and Views comment by *Hirth*, 2006]. Similarly, the conclusion of *Huang et al.* [2005] that the Transition Zone is wet was contradicted by *Yoshino et al.* [2008] who concluded that it is dry, which in turn was robustly challenged by *Karato* [2011]. To further confuse the issue, a study by *Romano et al.* [2009] suggest that small polaron conduction dominates in the Transition Zone rather than proton conduction, concluding that even if it is wet the water content cannot be detected electromagnetically.

[19] In a similar vein, recently *Naif et al.* [2013] used Poe's results [*Poe et al.*, 2010] to conclude that 800 ppm water would be required to explain the low resistivity observed in the asthenosphere just below the lithosphere-asthenosphere boundary (LAB) beneath the Cocos Plate, and that such high water content would invoke partial melting. (Such a large amount of water is also unreasonably high, based on petrological arguments [*Bai and Kohlstedt*, 1992; *Green et al.*, 2010].) Founded on invoking partial melting, the authors conclude that they had observed a melt channel at the LAB. However, had the authors adopted instead Karato's results [*Wang et al.*, 2006], they would only have required a far more reasonable 100–230 wt ppm

water in olivine to obtain 4–6 Ωm at 1400°C. This range of water content bounds the value of 180 wt ppm deduced by *Green et al.* [2010; corrected in *Green et al.*, 2011] for the amount of water carried by residual lherzolite in the mantle, so would appear to be a fully satisfactory and consistent alternative interpretation that does not require partial melt. (Although a very recent paper by *Fei et al.* [2013] concludes, contrary to prior studies, that a small amount of water (tens to hundred ppt) is insufficient to explain the minimum viscosity zone associated with the asthenosphere, which would lend support to the inference of *Naif et al.* [2013] that partial melt is required.)

[20] The models derived by the four labs for proton conduction in olivine at lithospheric conditions are given in Table 1, together with the arithmetic average of the anisotropic results of *Poe et al.* [2010] used by *Fullea et al.* [2011]. Also given in Table 1 is the model of *Jones et al.* [2012] that fits field data from the Jagersfontein (JAG) and Gibeon (GIB) kimberlite fields in southern Africa where there are tight estimates of temperature, electrical conductivity, and water content at 100 km depth. All models are plotted in Figure 1 for a temperature of 740°C over the water content range of 0–2000 wt ppm (Figure 1a) and 0–200 wt ppm (Figure 1b). The latter range is the likely range of water content in olivine in the lithospheric mantle [*Peslier et al.*, 2010; *Baptiste et al.*, 2012]. Note that all of the measurements by *Poe et al.* [2010] were conducted at far higher water contents than observed in the lithospheric mantle and conjectured to exist in the sublithospheric upper mantle. For comparison and completeness, models are also listed in Table 1 of olivine in its high pressure forms, namely wadsleyite and ringwoodite.

[21] For intercomparison, the laboratory data in the various publications have either been normalized or extrapolated to a temperature of 740°C, and those values are plotted in Figure 1 and given in Table 2. In the case of the Karato group's data (black filled circles), published in the supporting information of *Wang et al.* [2006], the values at 740°C were derived using the reported model activation energy of 0.87 eV and the Karato model (with $\alpha = 0$), viz.

$$\ln(\sigma(T_{740})) = \left(\ln(\sigma(T_1)) + \frac{\Delta H_w}{kT_1} \right) - \frac{\Delta H_w}{kT_{740}} \quad (6)$$

[22] The values for the other data at 740°C were obtained by digitizing them off the regression models plotted in the respective publications. Also

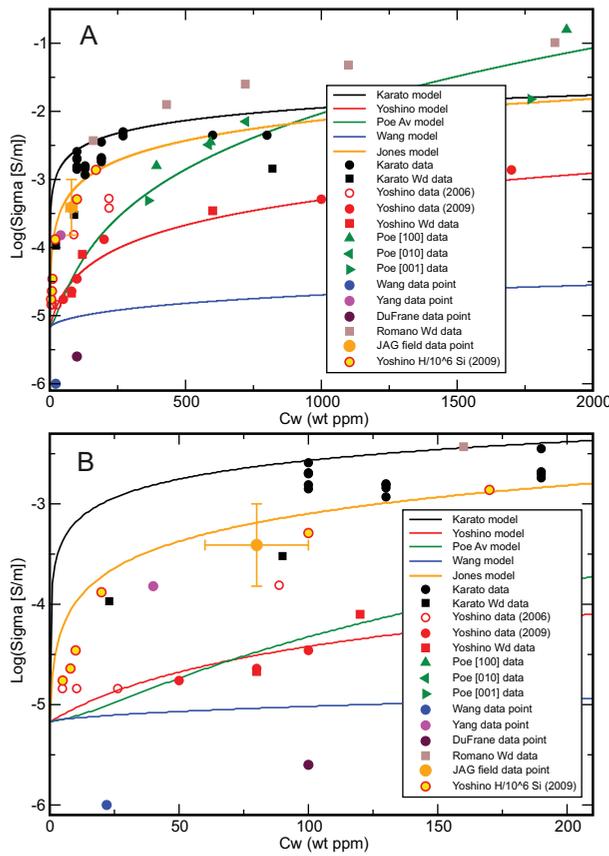


Figure 1. Models of proton conduction in olivine listed in Table 1 at a temperature of 740°C and the laboratory observations either calculated at 740°C or scaled off the regression lines in the plots for water content ranges of (a) 0–2000 wt ppm and (b) 0–200 wt ppm. Karato (black line): Wang *et al.* [2006]; Yoshino (red line): Yoshino *et al.* [2009]; Poe (green line): Poe *et al.* [2010], as averaged by Fullea *et al.* [2011]; Wang (blue line): Wang *et al.* [2008]; Jones (orange line): Jones *et al.* [2012]. Also shown as data points are inferred laboratory-determined values at 740°C listed in Table 2 based on interpolation or extrapolation of regression lines given in the respective publications, or recalculations in the case of Karato’s olivine estimates. (Olivine unless stated.) Karato (black circles): Wang *et al.* [2006]; Karato wadsleyite (black squares): Dai and Karato [2009]; Yoshino 2006 (open red circles): Yoshino *et al.* [2006]; Yoshino 2009 (filled red circles), Yoshino H/10⁶ Si (orange-filled red circles): Yoshino *et al.* [2009]; Yoshino wadsleyite (red squares): Yoshino *et al.* [2008]; Poe (green triangles, orientation indicates crystallographic direction): Poe *et al.* [2010]; Wang peridotite (blue circle): Wang *et al.* [2008]; Yang (purple circle): Yang [2012]; DuFrane (dark brown circle): Du Frane and Tyburczy [2012]; Romano wadsleyite (light brown circle): Romano *et al.* [2009]. Also shown is the field-based estimate of Jones *et al.* [2012] (orange data point with error bars) for a depth of 100 km below the Jagersfontein kimberlite field in the western part of the Kaapvaal Craton, South Africa.

plotted in Figure 1 is the single data point for the lithospheric conductivity and water content at 100 km beneath Jagersfontein on the Kaapvaal Craton, South Africa discussed in Jones *et al.* [2012] (orange point with error bounds). In addition, the conductivity values from Yoshino *et al.* [2009] are plotted twice: (i) based on the water contents as reported in wt% (solid red circles) and (ii) with “corrected” water contents consistent with the listings in H/10⁶ Si of Table 1 that are a factor of 10 times lower than those in wt% (orange-filled red circles).

[23] All of the proton conductivity models were shown by Jones *et al.* [2012] not to fit petrological and magnetotelluric field observations at Jagersfontein (JAG) and also at the Gibeon kimberlite field in Namibia, and Jones *et al.* [2012] proposed a new model based on fits to field observations that combined the two formalisms by using a nonunity value for r and a nonzero value for α , albeit both with large errors associated with both of them. All of the original laboratory data points, as extrapolated to 740°C shown in Figure 1, are outside to well outside the error bounds of the JAG data point, but it is astounding just how spectacularly well the “corrected” data points of Yoshino *et al.* [2009] (orange-filled red circles) are consistent with the JAG value and are fit spectacularly well by the model of Jones *et al.* [2012] (orange line, Figure 1).

3. Meyer-Neldel Considerations

[24] Following the Meyer-Neldel rule of equation (2), then from equation (5) it must follow that

$$\ln(\sigma_{op} C_w^r) = a + b \left(\Delta H_w - \alpha C_w^{1/3} \right), \quad (7)$$

where a and b are the MNR intercept and gradient parameters. Any variation in the activation enthalpy due to varying water content must be consistent with a concomitant variation in the pre-exponent to be consistent with the MNR. This means that to be MNR consistent, α cannot be zero, i.e., from an MNR perspective the formalism of Karato and coworkers is certainly incorrect as it is MNR inconsistent.

[25] We note that Karato’s experiments were conducted at low water contents with most focus on data at 100 wt ppm H₂O, whereas those of Yoshino were higher (up to 500 wt ppm), and of Poe were a lot higher (400–2000 wt ppm) (Table 2 and Figure 1). Due to the cube-root term on C_w in the activation energy, sensitivity to and resolution of

Table 2. Laboratory Data of Conductivity With Varying Water Content at 740°C^a

Reference	Water Content (ppm)	σ (S/m)	Temperature (°C)	$\text{Log}_{10}(\sigma \text{ (S/m)})$ at 740°C	Comments	
<i>Wang et al.</i> [2006]	270	0.0025	687	-2.36	K428	
	270	0.0386	1000	-2.30	K428	
	800	0.0010	608	-2.35	K462	
	600	0.0009	600	-2.35	K468	
	190	0.0273	1000	-2.45	K488	
	190	0.0032	800	-2.74	K488	
	190	0.0014	700	-2.68	K488	
	190	0.0004	600	-2.70	K488	
	130	0.0133	1013	-2.80	K492	
	130	0.0055	898	-2.84	K492	
	130	0.0026	795	-2.81	K492	
	130	0.0007	690	-2.93	K492	
	100	0.0108	1000	-2.85	K500	
	100	0.0060	900	-2.81	K500	
	100	0.0036	800	-2.69	K500	
	100	0.0017	700	-2.59	K500	
100	0.0004	600	-2.70	K500		
<i>Yoshino et al.</i> [2006]	5			-4.84	The three lines all cross at around 750°C	
	10			-4.84		
	26			-4.84		
	89			-3.81		
	218			-3.42		
	217			-3.28		
<i>Wang et al.</i> [2008]	22			-6.00		
<i>Yoshino et al.</i> [2008]	80			-4.67	Wadsleyite	
	120			-4.10		
	600			-3.46		
<i>Dai and Karato</i> [2009]	23			-3.97	Wadsleyite	
	90			-3.52		
	820			-2.84		
	2200			-2.53		
<i>Romano et al.</i> [2009]	400			-2.23	Wadsleyite	
<i>Poe et al.</i> [2010]	383			-2.80	[100]	
	592			-2.45		
	1903			-0.80		
	585			-2.49	[010]	
	722			-2.15		
	363			-3.31	[001]	
	1771			-1.82		
	2215			-1.57		
	50 → 5				-4.76	
	80 → 8				-4.64	
100 → 10				-4.46		
200 → 20				-3.88		
1000 → 100				-3.29		
1700 → 170				-2.86		
<i>Du Frane and Tyburczy</i> [2012]	100			-5.6	Based on diffusion calculation	
<i>Yang</i> [2012]	40			-3.82	Measurements made on all three axes, but gave same result	

^aData from *Wang et al.* [2006] calculated to 740°C with an assumed value of activation energy of 3.00. All others obtained from the plotted curves in the respective publications. All data plotted in Figure 1.

^bWater contents in *Yoshino et al.* [2009] reported in both wt% and H/10⁶ Si, with the latter a factor of 10 smaller than the former.

the value of α only comes at high values of water content where $\alpha C_w^{1/3}$ becomes a measurable fraction of ΔH_w , so it is not surprising that Karato's group were able to fit their experimental data without requiring the $\alpha C_w^{1/3}$ term. At low values of water content, of order those found typically in the cratonic mantle (20–100 ppm), then Yoshino and Poe's formulation effectively only differs from Karato's through the exponent r on C_w in the pre-

exponent term. Yoshino and Poe assume it is unity, whereas Karato fitted his data with an r of 0.62 ± 0.15 . This is examined further below.

[26] Rearranging equation (7) yields for α

$$\begin{aligned} \alpha &= (a + b\Delta H_w - \ln(\sigma_{0p} C_w^r)) / b C_w^{1/3} \\ &= (a + b\Delta H_w - \ln(\sigma_{0p}) - r \ln(C_w)) / b C_w^{1/3}, \end{aligned} \quad (8)$$

and clearly α is a function of water content C_w , so it should not be surprising that Yoshino's isotropic conductivity estimate of 0.16, made for moderate values of C_w , is very different from Poe's anisotropic conductivity estimates of 1.18, 1.43, and 0.70, along the [100], [010], and [001] crystallographic axes, respectively, made at high values of C_w . Also note that α is directly proportional to $-r$.

[27] Representative values of the constants ΔH_w and $\sigma_{0,p}$ are 0.91 eV and 1000 S/m (Table 1), and of the MNR intercept a and slope b for high temperature proton conduction in olivine are -4.75 and $+7$, respectively (see above). Thus typically

$$\begin{aligned}\alpha &= (-4.75 + 6.37 - 6.9 - r \ln(C_w)) / 7C_w^{1/3} \\ &\approx (-5.3 - r \ln(C_w)) / 7C_w^{1/3},\end{aligned}\quad (9)$$

or alternatively,

$$r \approx (-5.3 - 7\alpha C_w^{1/3}) / \ln(C_w). \quad (10)$$

[28] For $\alpha = 0.00$, which is the assumption of the Karato and Wang groups, then

$$r = -5.3 / \ln(C_w), \quad (11)$$

i.e., the estimates of r that are determined in lab studies will be a function of the water content analyzed and will not be a constant value. For water content of 100 wt ppm, for which most of the data exist of *Wang et al.* [2006], then $r = 1.15$, which is well outside the error range of the r value that *Wang et al.* [2006] determined (0.62 ± 0.15) and is greater than the value derived by *Jones et al.* [2012] of 0.86. However, at higher or lower water contents then the estimate of r varies, i.e., for $C_w = 40$ wt ppm then $r = 0.96$, and for $C_w = 200$ wt ppm then $r = 1.35$.

[29] Alternatively, for an assumption of $r = 1.00$, which is that of the Yoshino and Poe groups, then

$$\alpha = (-5.3 - \ln(C_w)) / 7C_w^{1/3}, \quad (12)$$

i.e., in a similar manner, the estimates of α that are determined in lab studies will be a function of the water content analyzed, and also will not be a constant value.

[30] This examination clearly demonstrates that the general formalism of equation (5) needs to be modified to be consistent with the MNR. One can neither adopt a constant r nor a constant α and obtain an MNR consistent formalism valid over a broad range of water contents.

[31] There are essentially three choices on how to do this, given extant formalisms:

[32] 1. Assume that the Karato formalism (C_w^r in the preexponent term) is correct, and require the activation energy term to be MNR consistent with it, or

[33] 2. Assume that the Yoshino/Poe formalism ($-\alpha C_w^{1/3}$ added to the activation enthalpy term) is correct, and require the preexponent term to be MNR consistent with it, or

[34] 3. Assume that neither is correct, and develop a new formalism that is MNR consistent.

3.1. Meyer-Neldel Consistent Yoshino/Poe Formalism

[35] Starting from the premise that the Yoshino and Poe modification, of adding the term $-\alpha C_w^{1/3}$ to the activation energy is correct, and there is some support for this from recent ab initio numerical experiments [*Panero et al.*, 2013], then we can write proton conduction as a function of water content and temperature as

$$\sigma_p(C_w, T) = \sigma_{0p} f_{YP}(C_w) \exp\left(\frac{-(\Delta H_w - \alpha C_w^{1/3})}{kT}\right) \quad (13)$$

where $f_{YP}(C_w)$ is an unknown function of C_w in the preexponent term that is derived to be consistent with the MNR.

[36] Following the Meyer-Neldel Rule, then

$$\ln(\sigma_{0p} f_{YP}(C_w)) = a + b(\Delta H_w - \alpha C_w^{1/3}), \quad (14)$$

where a and b are the MNR intercept and gradient as before, from which

$$f_{YP}(C_w) = \exp\left(a + b(\Delta H_w - \alpha C_w^{1/3}) - \ln(\sigma_{0p})\right), \quad (15)$$

[37] And the proton conduction equation for Yoshino and Poe's formalism is

$$\begin{aligned}\sigma_p(C_w, T) &= \sigma_{0p} \exp\left(a + b\left(\Delta H_w - \alpha C_w^{1/3}\right) - \ln(\sigma_{0p})\right) \\ &\quad \exp\left(\frac{-\left(\Delta H_w - \alpha C_w^{1/3}\right)}{kT}\right), \\ &= \exp\left(a + b\left(\Delta H_w - \alpha C_w^{1/3}\right)\right) \exp\left(\frac{-\left(\Delta H_w - \alpha C_w^{1/3}\right)}{kT}\right), \\ &= \exp(a) \exp\left(\frac{(bkT - 1)\left(\Delta H_w - \alpha C_w^{1/3}\right)}{kT}\right),\end{aligned}\quad (16)$$

which follows directly from equation (3). Clearly, the function $f_{YP}(C_w)$ in equation (15), which is the preexponent term in C_w (i.e., it does not contain σ_0), must contain the variable α in order to be internally consistent with the MNR. For the MNR intercept and gradient values for olivine small polaron and of proton conduction, we take $a = -4.75$, $b = 7.0$, and for the typical values of proton conduction we take $\Delta H_w = 0.91$ eV, and $\sigma_{0p} = 1000$ S/m, then

$$\begin{aligned}f_{YP}(C_w) &= \exp\left(-4.75 + 7.0\left(0.91 - \alpha C_w^{1/3}\right) - 6.9\right) \\ &\approx \exp(-5.3) \exp(-7\alpha C_w^{1/3}) \\ &\approx 0.005 \exp(-7\alpha C_w^{1/3}).\end{aligned}\quad (17)$$

[38] A plot of this function, scaled by C_w , is shown in Figure 2. Note that at low water content, then the function is dominated by C_w and is virtually independent of α , whereas for high water content, it is dominated by α and virtually independent of

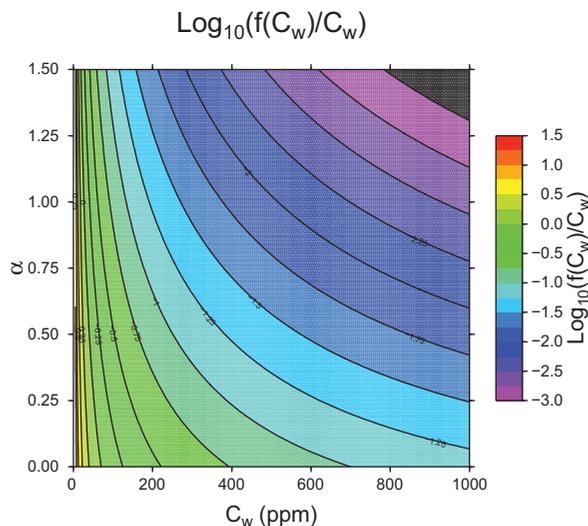


Figure 2. Variation of $f_{YP}(C_w)$, scaled by C_w , for the range $C_w = [0, 1000]$ wt ppm and $\alpha = [0, 1.5]$.

C_w . This explains why the Karato group did not need to use an α term as their experiments were on samples with low water contents (mostly at 100 wt ppm), whereas the Yoshino and Poe groups need an α term as their experiments were on samples with high water contents (up to 2200 wt ppm).

[39] Taking the values assumed above of $a = -4.75$, $b = 7.0$, and $\Delta H_w = 0.91$ eV, for an $\alpha = 0.16$ (Yoshino's fitted value), then

$$\sigma_p(C_w, T) = \exp(-4.75) \exp\left(\frac{(7.0kT - 1)(0.91 - 0.16C_w^{1/3})}{kT}\right).\quad (18)$$

[40] Function (18) is plotted as the red line in Figure 3a ($C_w = 0-2000$ wt ppm) and Figure 3b

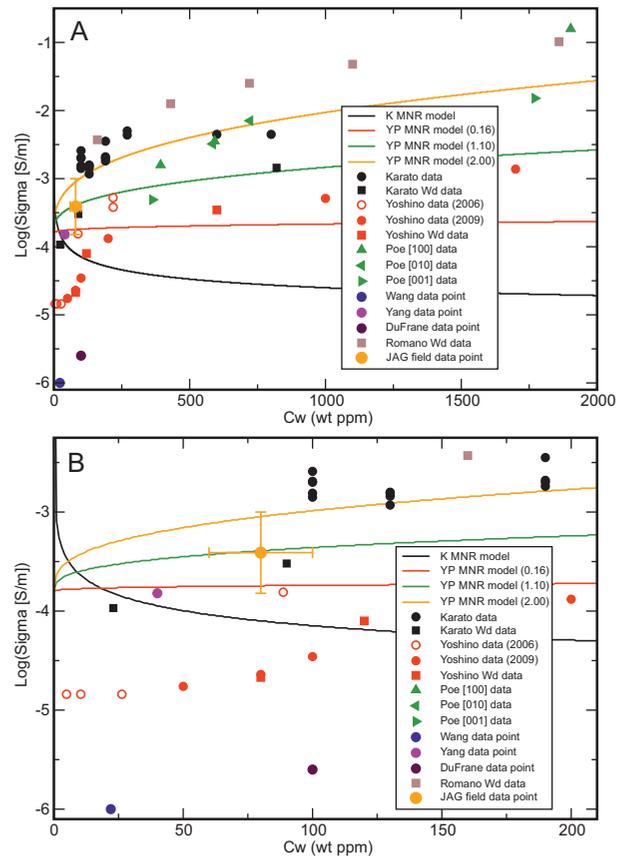


Figure 3. MNR-consistent models of proton conduction in olivine at 740°C for (a) $C_w = 0-2000$ wt ppm and (b) $C_w = 0-200$ wt ppm, assuming that the Karato formalism is correct (black line) and alternatively that the Yoshino (red line) and Poe (green line) formalism is correct (for differing values of α). Also shown are the laboratory data from Figure 1 (see caption for explanation), including the field-based estimate of Jones *et al.* [2012] (orange data point with error bars).

($C_w = 0\text{--}200$ wt ppm) for a temperature of 740°C , and is approximately

$$\begin{aligned}\sigma_p(C_w, 740) &\approx 0.0087 \exp\left(\frac{(7.0 \times 0.088 - 1)(0.91 - 0.16C_w^{1/3})}{0.088}\right), \\ &\approx 0.00016 \exp(0.69C_w^{1/3})\end{aligned}\quad (19)$$

(here k is in eV/K to allow ΔH_w to be expressed in eV).

[41] This function fits the JAG field data point, but is subsequently is far too “flat” with increasing water content, and does not replicate the response observed in the laboratory of significantly increasing conductivity with increasing water content. The gradient of the function can be modified by adopting a higher value of α , and Poe’s average value of 1.10 yields

$$\begin{aligned}\sigma_p(C_w, 740) &\approx 0.0087 \exp\left(\frac{(7.0 \times 0.088 - 1)(0.91 - 1.10C_w^{1/3})}{0.088}\right), \\ &\approx 0.00016 \exp(4.8C_w^{1/3}),\end{aligned}\quad (20)$$

which is also shown in Figures 3a and 3b (green line). The gradient can be further enhanced by increasing α to higher values, and a plot for $\alpha = 2.00$ is also shown in Figures 3a and 3b (orange line). This does replicate in a general way the behavior observed in the laboratories.

3.2. Meyer-Neldel Consistent Karato Formalism

[42] For the Karato/Wang formalism, we have to determine an expression for the activation energy $f_K(C_w)$ that is MNR consistent with the preexponent term $\sigma_0 C_w^r$. From the MNR relation (2), then

$$\ln(\sigma_0 C_w^r) = a + bf_K(C_w) \quad (21)$$

and the MNR-consistent proton conduction equation becomes

$$\sigma_p(C_w, T) = \sigma_{0p} C_w^r \exp\left(\frac{\ln(\sigma_{0p} C_w^r) - a}{bkT}\right) \quad (22)$$

[43] For assumed values of $a = -4.75$, $b = 7$, $\log_{10}(\sigma_{0p}) = 3.00$, and $r = 0.87$, this function plots as shown in Figures 3a and 3b (black line). This curve fails to replicate the observed increasing con-

ductivity with increasing water content, and indeed it shows exactly the opposite behavior.

3.3. Meyer-Neldel Consistent General Formalism

[44] Assume a function of water content $f_G(C_w)$ for the activation enthalpy term, the general MNR consistent proton conduction equation is

$$\begin{aligned}\sigma_p(C_w, T) &= \exp(a + bf_G(C_w)) \exp\left(\frac{-f_G(C_w)}{kT}\right), \\ &= \exp(a) \exp\left(\frac{(bkT - 1)f_G(C_w)}{kT}\right),\end{aligned}\quad (23)$$

which, for $a = -4.75$ and $b = 7$, is

$$\sigma_p(C_w, T) = 0.00865 \exp\left(\frac{(7kT - 1)f_G(C_w)}{kT}\right). \quad (24)$$

[45] The activation enthalpy function $f_G(C_w)$ can take any form, as long as it has the property that it fits the data. It is appropriate to appeal to solid state physics to define the form of $f_G(C_w)$, as done previously by Karato, Yoshino, and Poe. Unfortunately, the disparate observations shown in Figure 1 do not make it possible to definitively design an appropriate $f_G(C_w)$. However, we have above shown that the Yoshino/Poe activation enthalpy term of $\Delta H_w - \alpha C_w^{1/3}$, suggested by ab initio numerical experiments [Panero *et al.*, 2013], does have the approximate shape to fit the data with sufficiently large values of α of around 2.0.

4. Conclusions

[46] Laboratory measurements on minerals and rocks are crucially important for calibrating and limiting our interpretations of field data. However, when laboratories undertaking the same measurements are in fundamental disagreement and their results are inconsistent between them, then field-based scientists are in the unfortunate and unsatisfying position of having to choose between competing laboratory “truths,” often without the knowledge or abilities to make sensible choices. In some cases, the choices made can lead to dramatically different conclusions about the state of the Earth. This is true of measurements of proton conduction in mantle minerals, especially olivine, and the differences between the laboratories mean that field observations can be interpreted to imply either a dry or a wet mantle at various depths.

[47] In the case of proton conduction in rocks, there are two main “camps,” each modeling their data with a different formalism to introduce water-dependency in their Arrhenius equations used to fit their laboratory observations. One camp (Karato, Wang) uses an exponent on the water content term in the preexponent, whereas the other (Yoshino, Poe) adds a term to the activation enthalpy. Neither formalism is consistent with the Meyer-Neldel rule, nor indeed is the combined formalism used recently by Jones *et al.* [2012], that includes both terms (equation (5)), MNR consistent. We have shown that the fundamental difference between the two camps in their choice of formalism to fit their data is due to the ranges of water contents of the samples examined; for low water contents then it is sufficient, to within experimental error, to model the data by replacing the $-\alpha C_w^{1/3}$ in the activation energy term by a power term r on the water content in the preexponent term. This does not hold though at high water contents.

[48] Further, we have developed an MNR-consistent proton conduction equation in terms of the MNR intercept and gradient, and an activation enthalpy function. Small polaron conduction relations and also proton conduction in tetragonal phase crystal structure suggest values of the MNR intercept and gradient of -4.75 and 7.00 , respectively, although these do need further validation and verification. The general form of the activation enthalpy function, $f_G(C_w)$, can adopt that suggested by Yoshino and Poe of $\Delta H_w - \alpha C_w^{1/3}$, as supported by ab initio experiments, provided α takes large values (around 2.00). This also needs further validation and verification.

[49] We will not progress further in this subject, and our interpretations of our field data are seriously hampered, until there is greater consensus between the laboratories making these measurements. Plotting all of the data from the laboratories at the same temperature indicates the discrepancies between them (Figure 1). Competing statements made in Karato and Wang [2013] and Yoshino and Katsura [2013] indicate there is still much work to be done in reconciling the differences. The recent suggestion of F. Gaillard (personal communication, 2013) and Karato and Dai [2013] that the times 10 discrepancy in the water contents of the samples listed in H/10⁶ Si compared to wt% in Table 1 of Yoshino *et al.* [2009] is the source of the discrepancy, and that when the water contents are taken in H/10⁶ Si there is reasonably close agreement between the two labs of Karato and Yoshino is opposed by T. Yoshino (personal com-

munication, 2013) who insists that the values in wt% are the correct ones. Field data do however give support to the contention of F. Gaillard (personal communication, 2013) and Karato and Dai [2013]—compare the orange point and orange model line with the orange-filled red data points in Figure 1. However, even when these laboratories are reconciled, their formalisms are still not MNR consistent.

[50] We have outlined here a general formalism that should be adopted by all laboratories to ensure that the specific parameterization adopted to fit the laboratory data is consistent with the Meyer-Neldel rule. This MNR-consistent formalism is applicable not only for proton conduction in olivine, but to all conduction processes in all rocks and minerals, and indeed to all processes that are being described by an Arrhenius equation, and should similarly be adopted by the laboratory community. Although the evidence is mounting that the Meyer-Neldel rule is valid for more and more phenomena that can be described by an Arrhenius equation, there is no requirement for the laboratory community to accept the MNR, especially as it does have its detractors, but if the community wishes to be consistent with the MNR, then the formalism used for fitting the laboratory data must reflect that.

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