Permeability Studies Applied to Grain Boundary Diffusion in Alumina Scales

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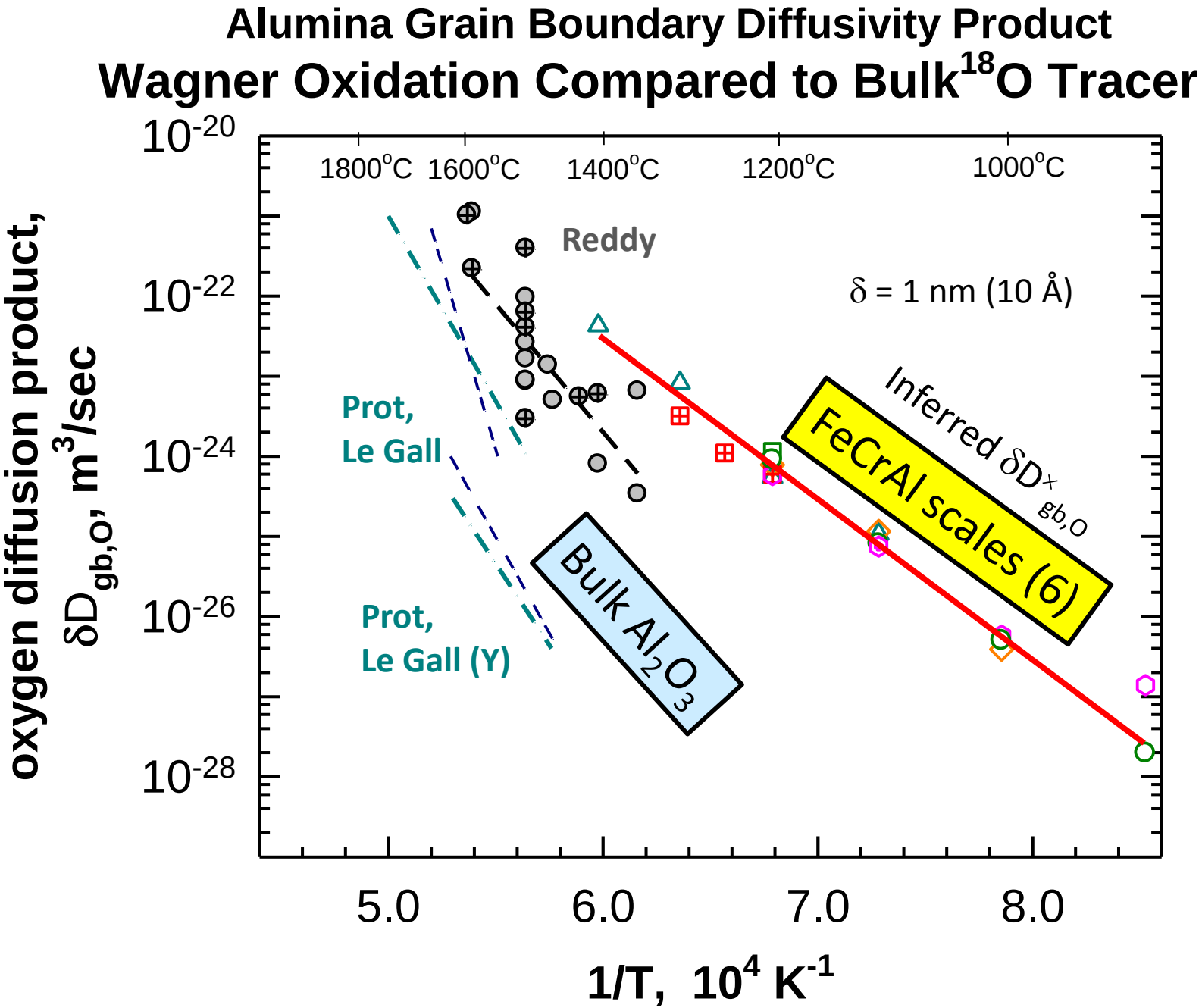
Alumina Scale Growth Mechanisms: Signposts along a 40 year journey

1. **Bulk** Al_2O_3 vs Al_2O_3 **scale** diffusivity
2. **Oxygen** inward vs **Aluminum** outward (n-type vs p-type)
3. Short circuit **grain boundary** diffusion (grain growth)
4. 'cubic' or **sub-parabolic** growth rates
5. **^{18}O tracer** (double oxidation) studies (NRA, SIMS profiles)
6. **Activation energies** (Arrhenius plots of log k_p vs 1/T)
7. Growth **stress**; creep relaxation
8. **Dopant** effects on defects, transport, and morphology
9. **pO_2** effects on σ_{el} , σ_I, $[V_o^{\circ\circ}]$, $[V_{Al}^{\prime\prime\prime}]$, D_O, D_{Al}

Objectives

- Introduce permeability, $\delta D_{gb,O,Al}$ equations
- New Wagner solutions
- Compare $k_{p,i}$ (predicted, measured, literature)
- Compare $\delta D_{gb,O}$
  predicted: permeability vs oxidation
  measured: ^{18}O literature)
- Recap, new insights
- Epilogue: MDC150L Ni(Pt)Al coating


Alumina Grain Boundary Diffusivity Product
Wagner Oxidation Compared to Bulk 18O Tracer
oxygen diffusion product, δDgb,O, m3/sec
10-20
10-22
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10-28
1800°C
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Reddy
δ = 1 nm (10 Å)
Prot, Le Gall
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Bulk Al2O3
Inferred δDx gb,O
FeCrAl scales (6)
5.0
6.0
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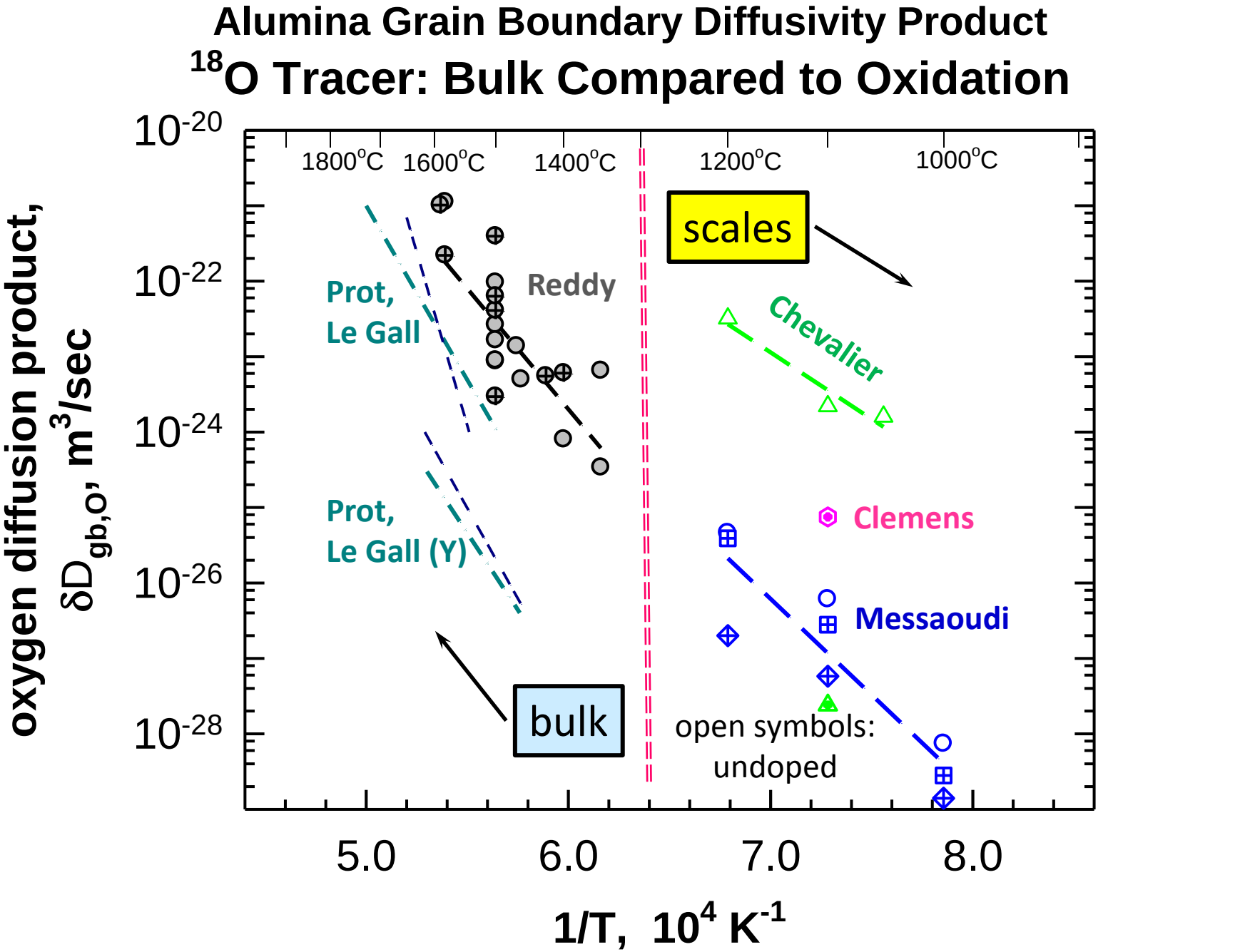
1/T, 10^4 K^-1


Alumina Grain Boundary Diffusivity Product
18O Tracer: Bulk Compared to Oxidation
oxygen diffusion product, δDgb,O, m3/sec
10-20
10-22
10-24
10-26
10-28
1800°C
1600°C
1400°C
1200°C
1000°C
scales
Reddy
Prot, Le Gall
Chevalier
Clemens
Prot, Le Gall (Y)
Messaoudi
bulk
open symbols: undoped
5.0
6.0
7.0
8.0
1/T, 10^4 K^-1

Wagner Model (from Kofstad)

$$k_{p,\text{instant}} = 2x\frac{dx}{dt} = \int_{P_{O_2},\text{interface}}^{P_{O_2},gas} \left(3/2 D_{eff,Al} + D_{eff,O}\right) d\ln P_{O_2}$$

GOAL: $k_p \leftrightarrow D_{Al,\,O}(Al_2O_3)$

Grain Size Affects D_{eff}

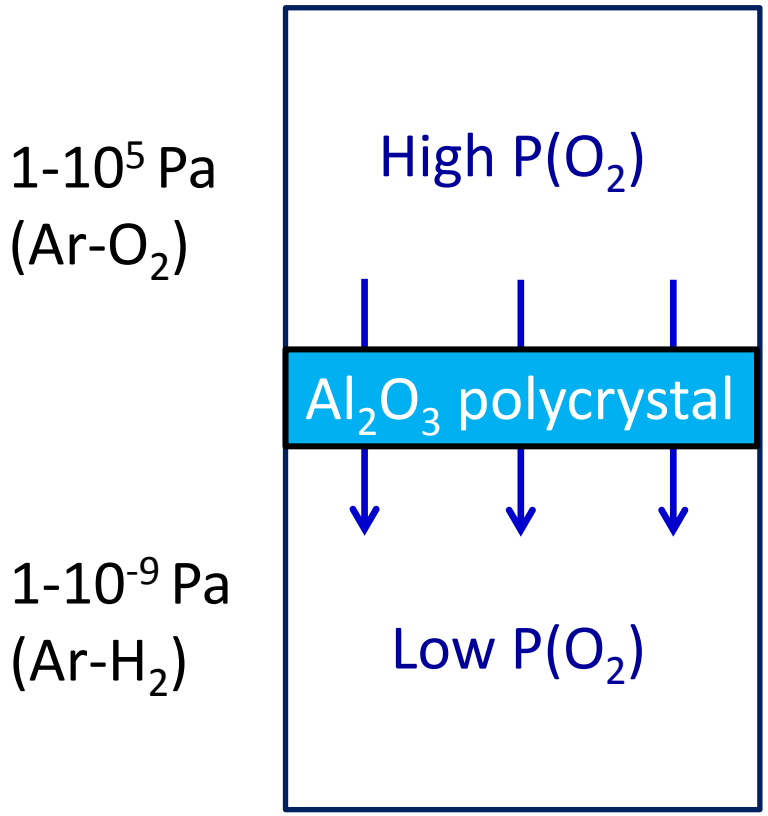
$$D_{eff} = (1 - f)D_l + f(D_{gb})$$

$$D_{eff} \approx fD_{gb} = \frac{2\delta D_{gb}}{G_i}$$

$$G_i \ (grain\ size) \propto T, t$$

Alumina Permeability Studies:

Wada, Matsudaira, Kitaoka; JCS-Japan 119 (2011) 832-839



Vary I or II

Measure P(H_2O)

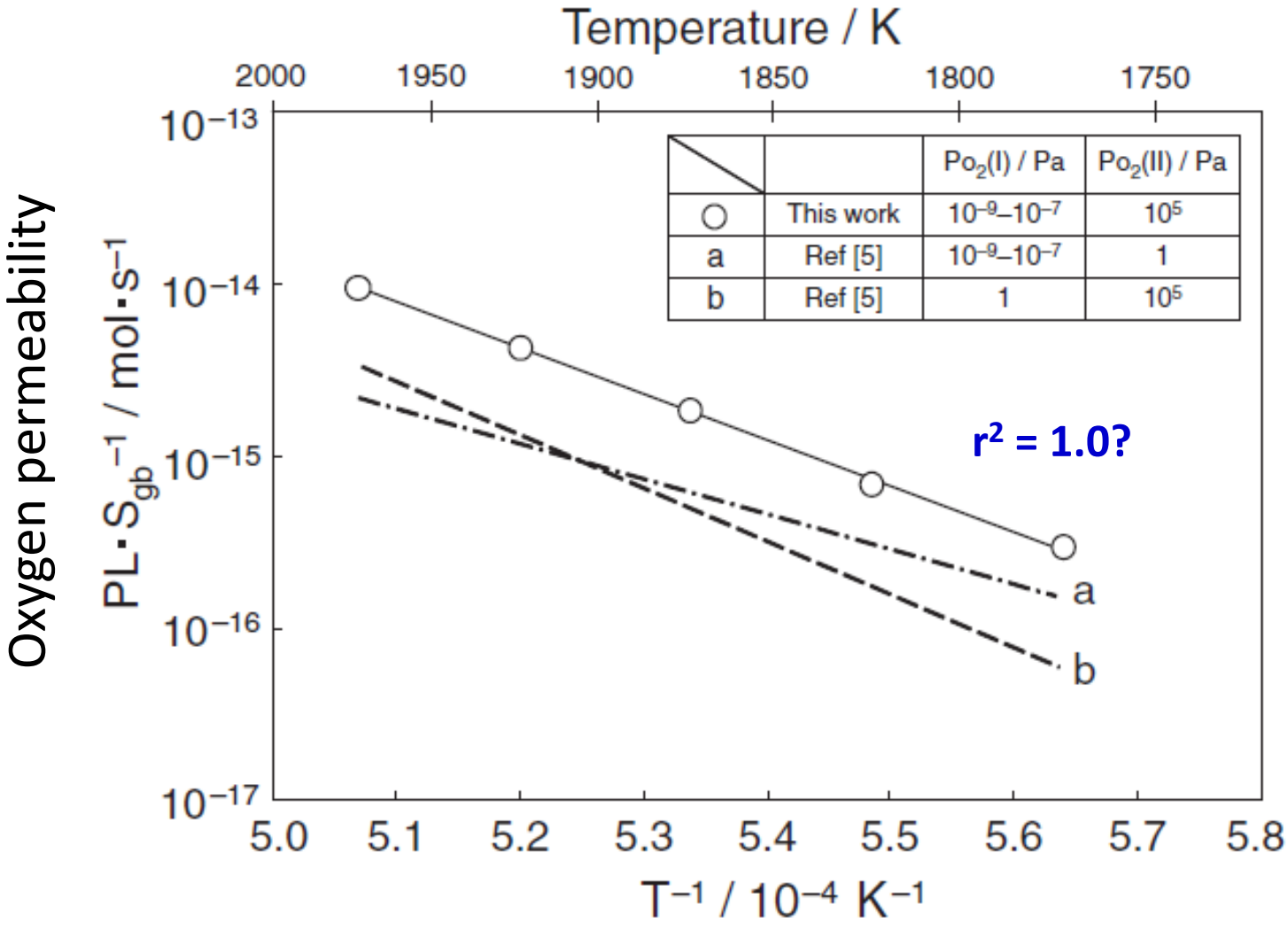
Measure P(O_2)

Calculate *P, J,* μ_O, δD_{gb}

(vs depth!)

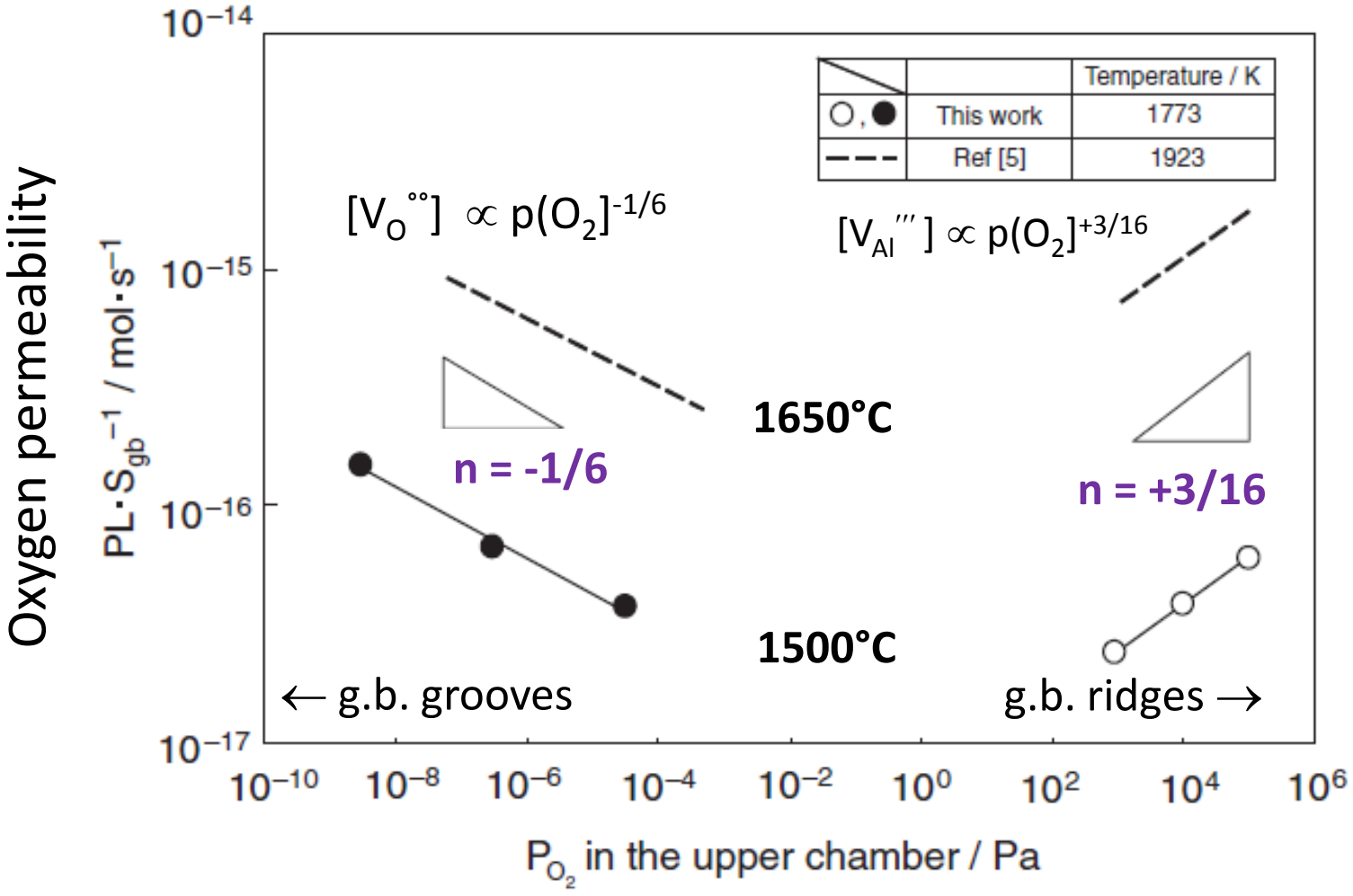
Alumina Permeability Studies: **Temperature Effects**

Wada, Matsudaira, Kitaoka; JCS-Japan 119 (2011) 832-839



Alumina Permeability Studies: $P(O_2)$ Effects

Wada, Matsudaira, Kitaoka; JCS-Japan 119 (2011) 832-839



δD_{gb} Measured from Alumina Permeability Studies

Wada, Matsudaira, Kitaoka; JCS-Japan 119 (2011) 832-839:

$$\delta D_{gb,O} = 2.207 \times 10^{-9} \exp\left(\frac{-467\ kJ}{RT}\right) \left(P_{O_2,low}\right)^{-1/6} \quad m^3/s$$

$$\delta D_{gb,Al} = 2.475 \times 10^{-5} \exp\left(\frac{-604\ kJ}{RT}\right) \left(P_{O_2,high}\right)^{3/16} \quad m^3/s$$

Wagner – Permeability Model (Oxygen)

$$k_{p,\text{instant}} = \int_{P_{O_2},\text{interface}}^{P_{O_2},gas} \frac{2A\exp(-Q/RT)}{G_i} P_{O_2}^{-1/6} d\ln P_{O_2}$$

Obtain $k_{p,i}$, δD_{gb} from eachother:

Oxygen (Primary) Contribution ($P_{O2,\ interface}$)

$$k_{p,i,O} = \frac{12\ \delta D^{W-W}_{gb,O,\,\mathrm{interface}}}{G_i}$$

$$or \quad k^{\times}_{p,i,O} = \frac{2\delta D^{\times}_{gb,O}\ \Delta \ln P_{O_2}}{G_i}$$

Aluminum Contribution ($P_{O2,\,gas}$)

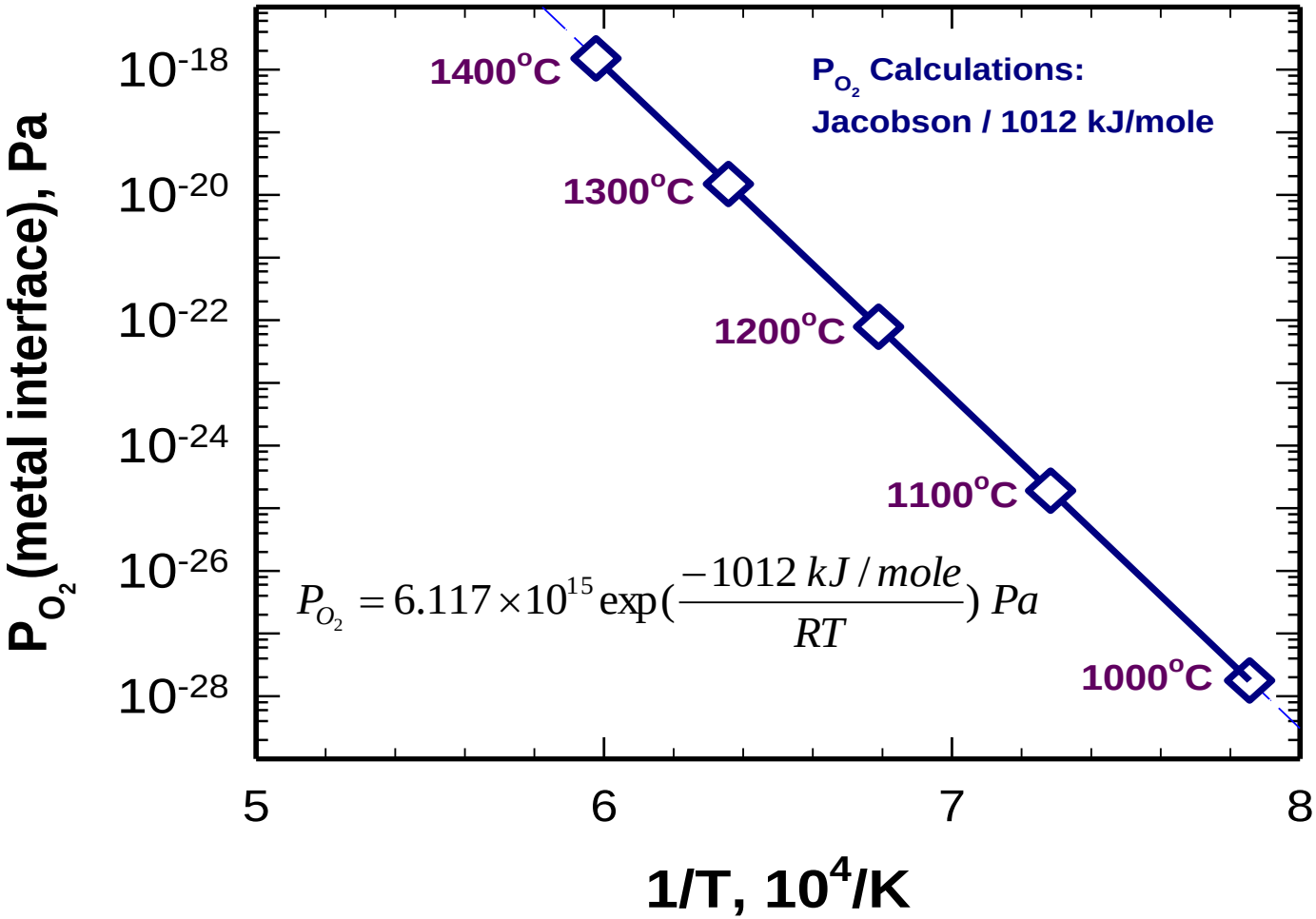
$$k_{p,i,Al} = \frac{16\,\delta D^{W-W}_{gb,Al,gas}}{G_i}$$

$$or \quad k^{\times}_{p,i,Al} = \frac{3\,\delta D^{\times}_{gb,Al}\;\Delta \ln P_{O_2}}{G_i}$$

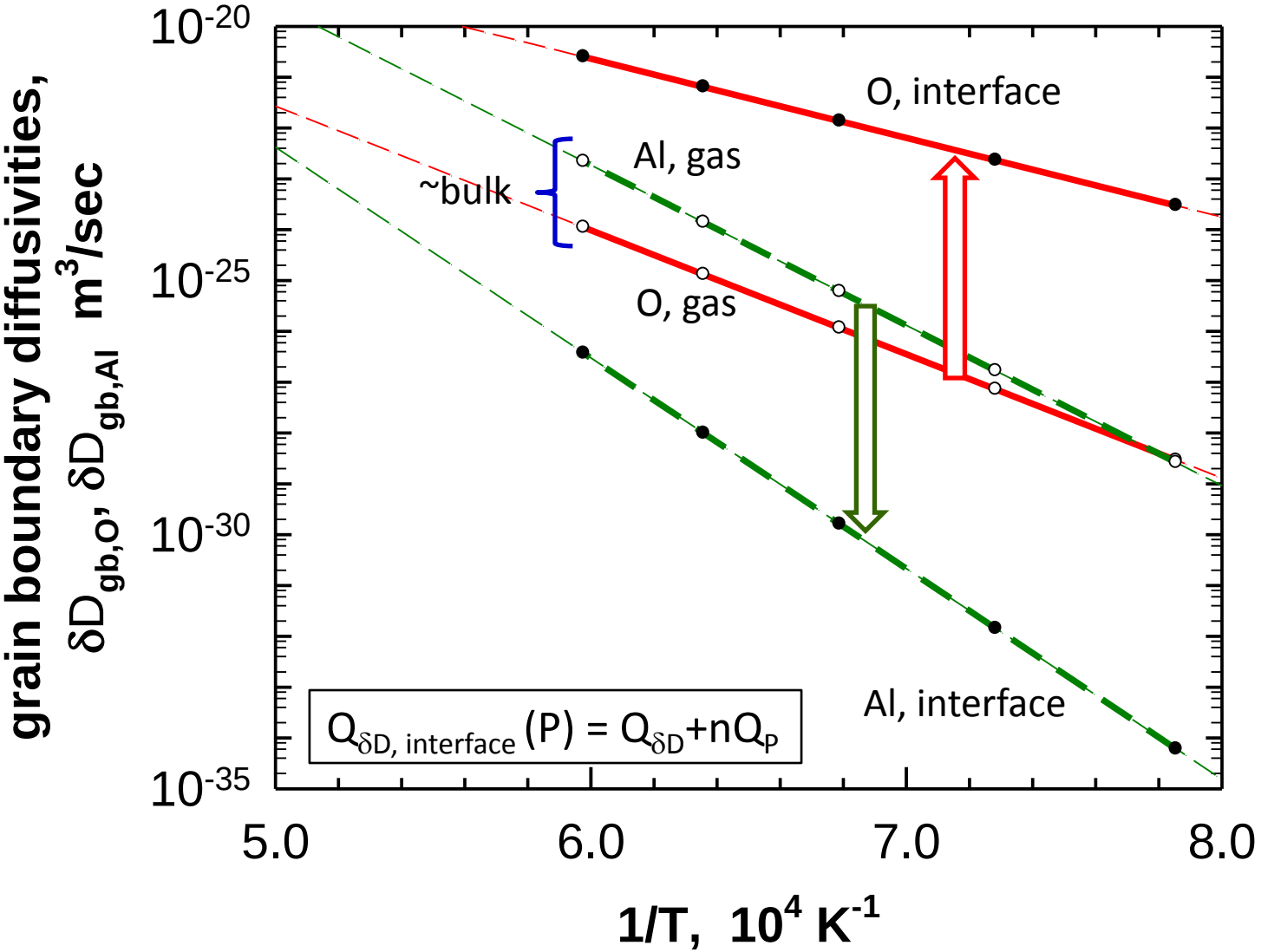
Equilibrium P(O_2) for FeCrAl(Zr) Oxidation Predictions

$$2Al + \tfrac{3}{2}O_2 = Al_2O_3$$

$$K_{eq} = 1/(a_{Al})^2(P_{O_2,equil})^{3/2}$$



Grain Boundary Diffusivity Product
Predictions for FeCrAl Scales vs Bulk Alumina



$$Q_{\delta D\ interface} = Q_{\delta D,\ gas} + nQ_{P,eq}$$

$Q_{P,eq}$ = 1012 kJ/mole

position	A_i (m^3/s)	Q_i (kJ/mole)	n_i
O, gas	4.23E-10	467	-1/6
O, interface	5.16E-12	**298**	-1/6
Al, gas	1.59E-04	604	+3/16
Al, interface	2.26E-02	**794**	+3/16

Measured k_p vs Predicted
(Permeability $\delta D_{gb,O}$)

$$\Pi_i = k_{p,i} \cdot G_i = 12\delta D_{gb,O,interface}$$

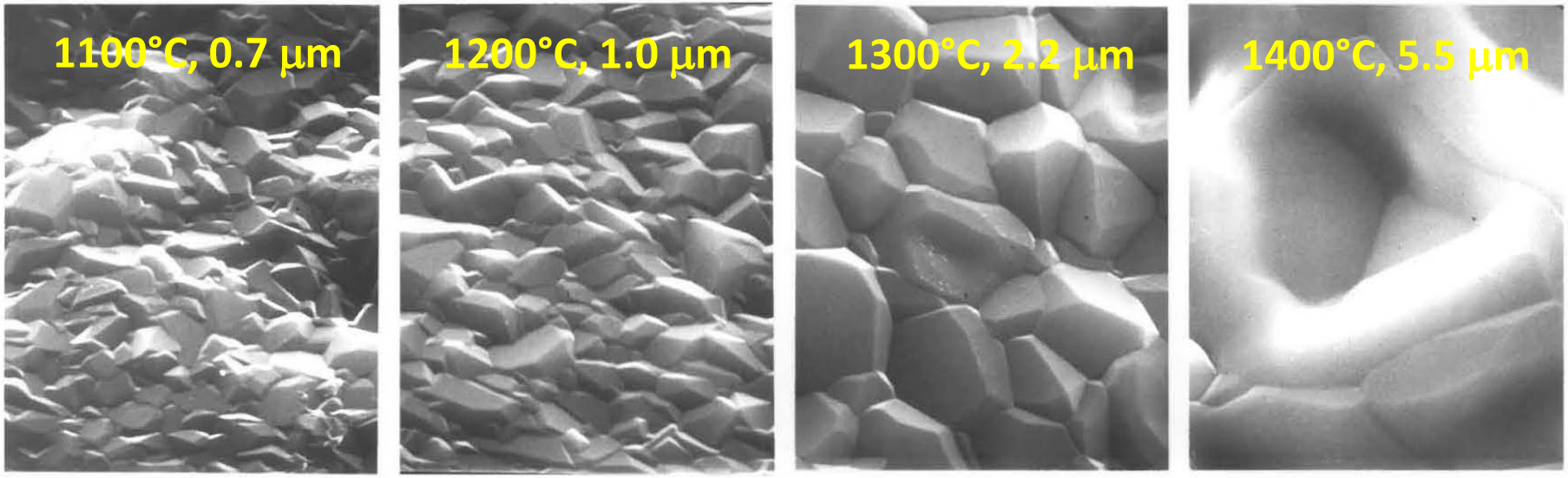
vs FeCrAl (Zr) Isothermal Oxidation

x_i (mg/cm^2), dx/dt, G_i for 25 samples

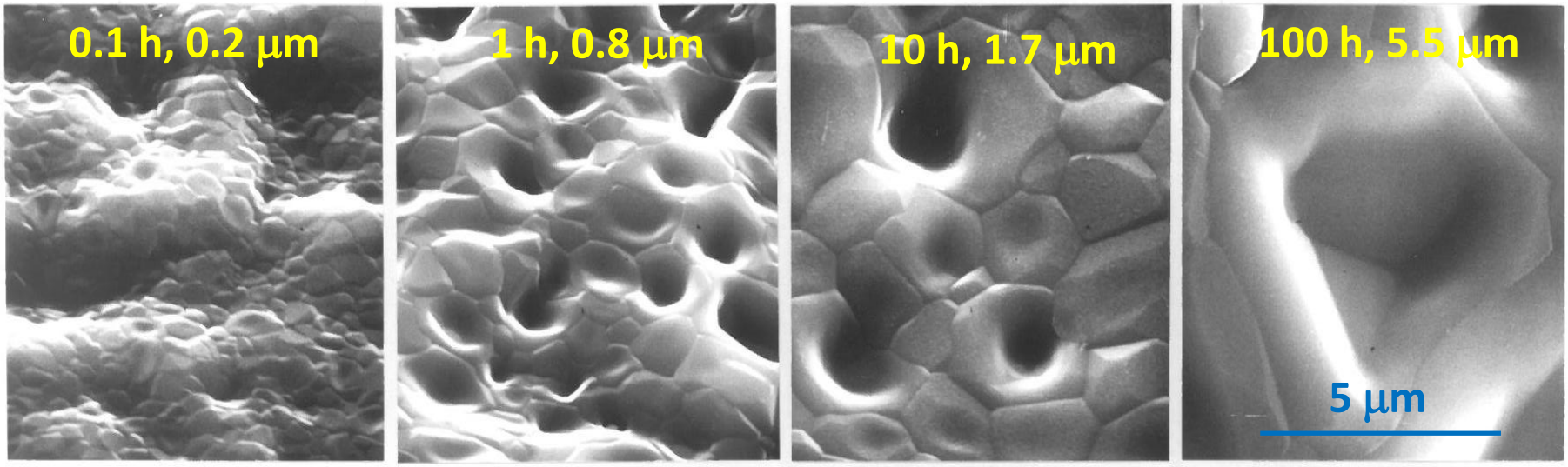
hours	1100°C	1200°C	1300°C	1400°C
0.1				
1				
10				
50				
100				
200				failed
500				
1000			failed	

Al_2O_3 Scale Underside Stripped from FeCrAl(Zr)

(A) 100 h

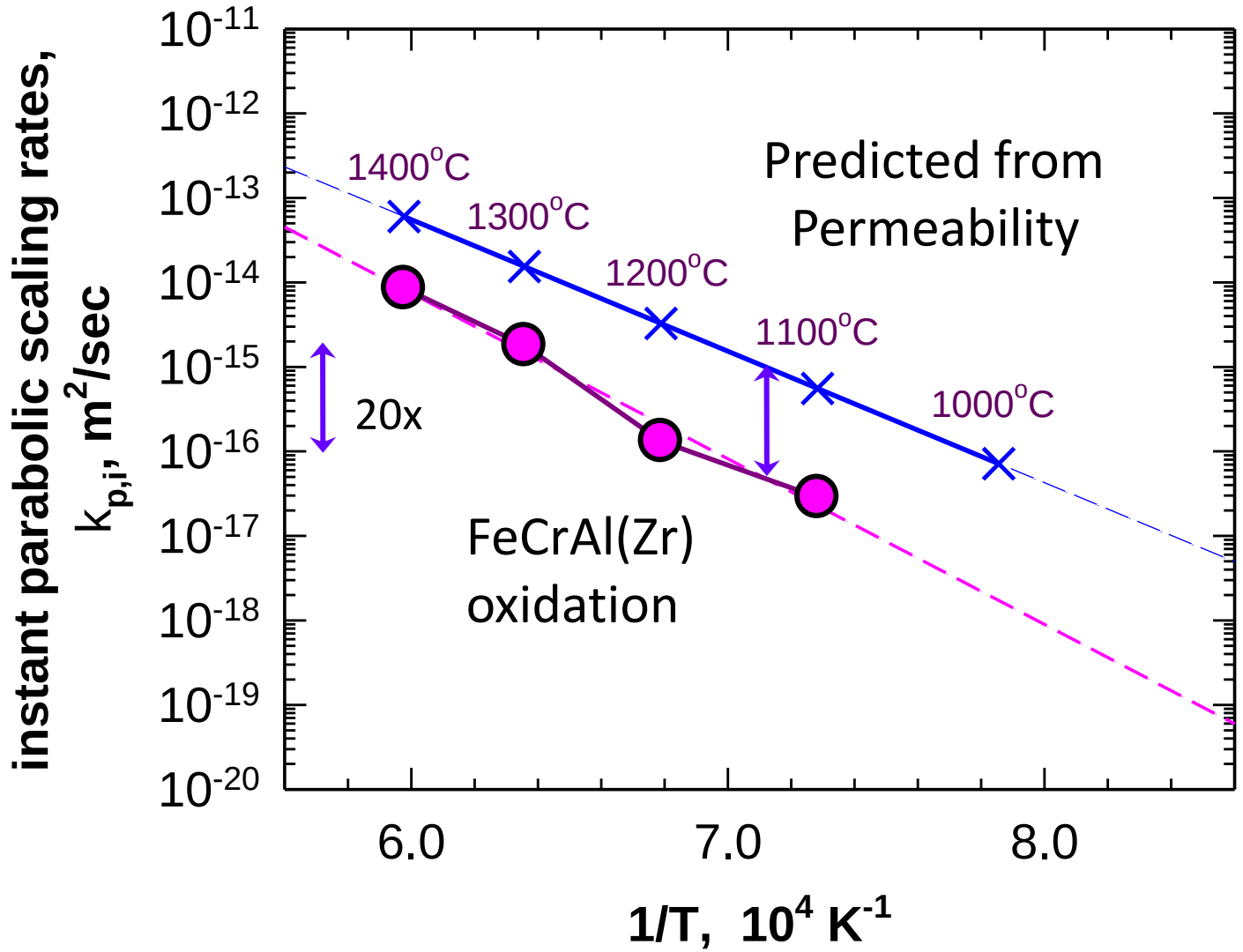


(B) 1400°C,



Alumina Scale Growth Rates on FeCrAl(Zr)
$k_{p,i}$ Measured and Predicted from Permeability

$\delta D_{gb,O}$; $k_{p,i}$ at GS =0.5μm



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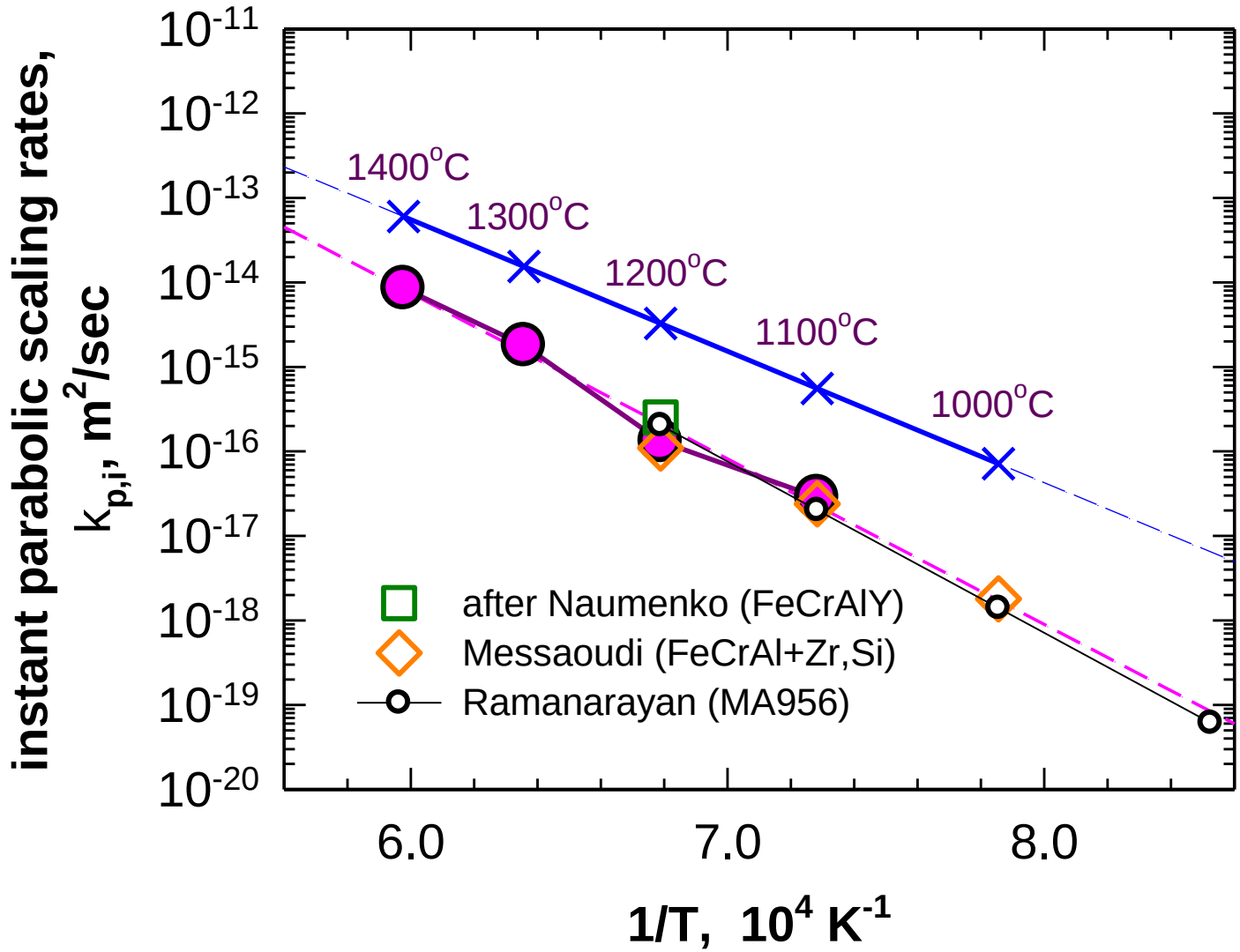
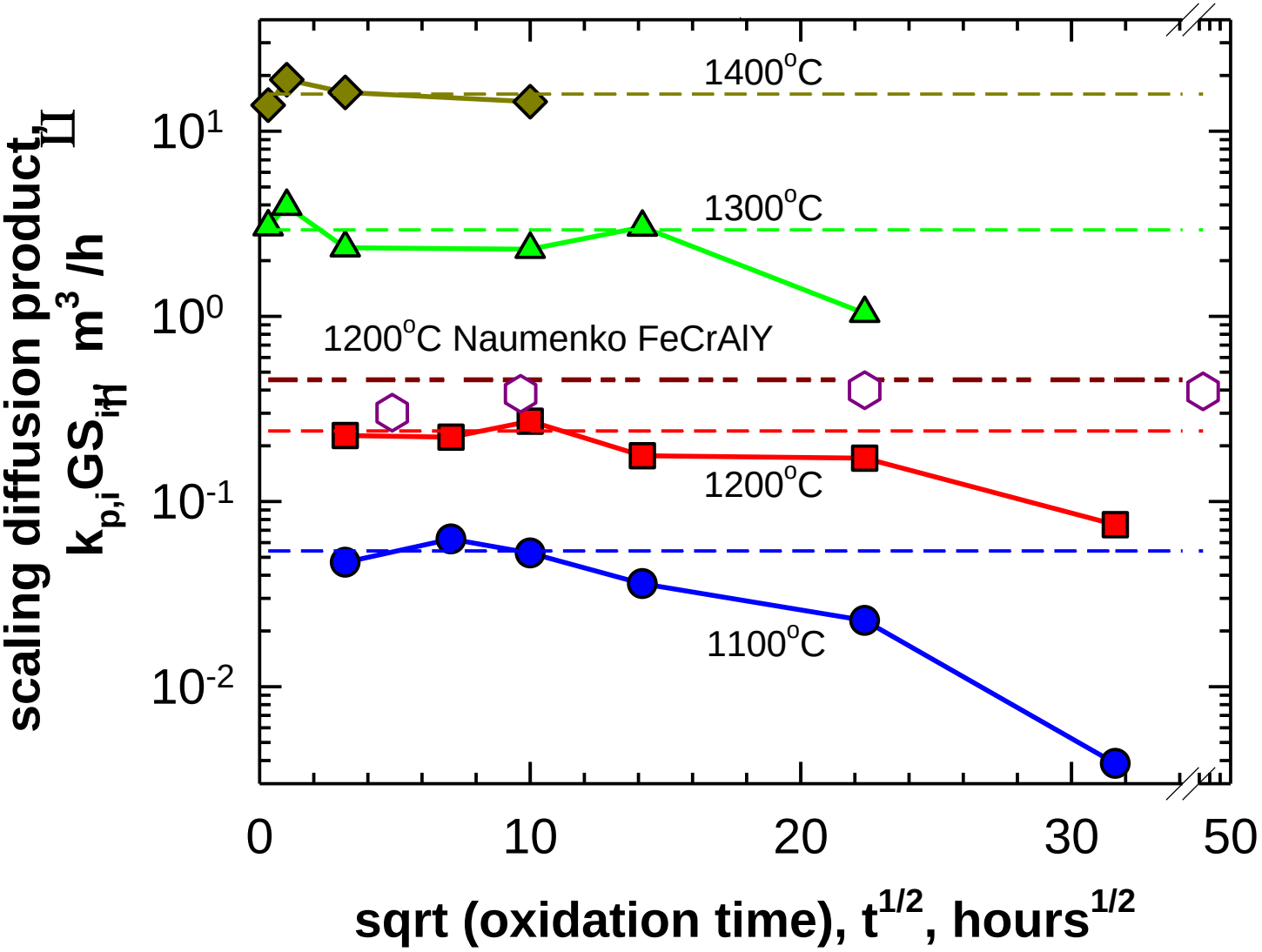


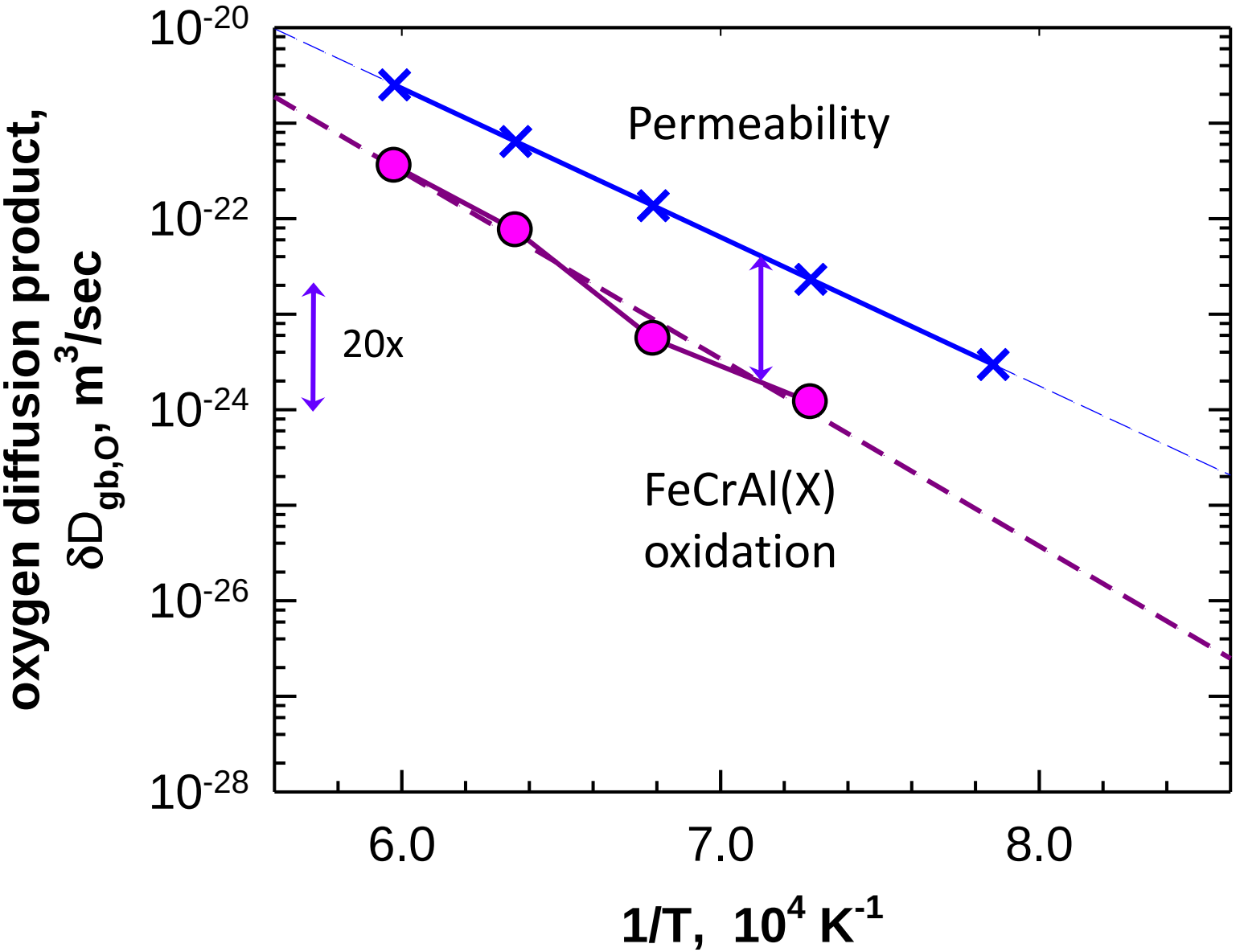
Predict $\delta D_{gb,O}$ from k_p

$$\Pi_i = k_{p,i} \cdot G_i = 12 \delta D_{gb,O,interface}$$

"Invariant" Scaling Product, Π, from FeCrAlZr Oxidation Rates



Scale Grain Boundary Diffusivity Product
Oxidation Compared to Permeability Predictions



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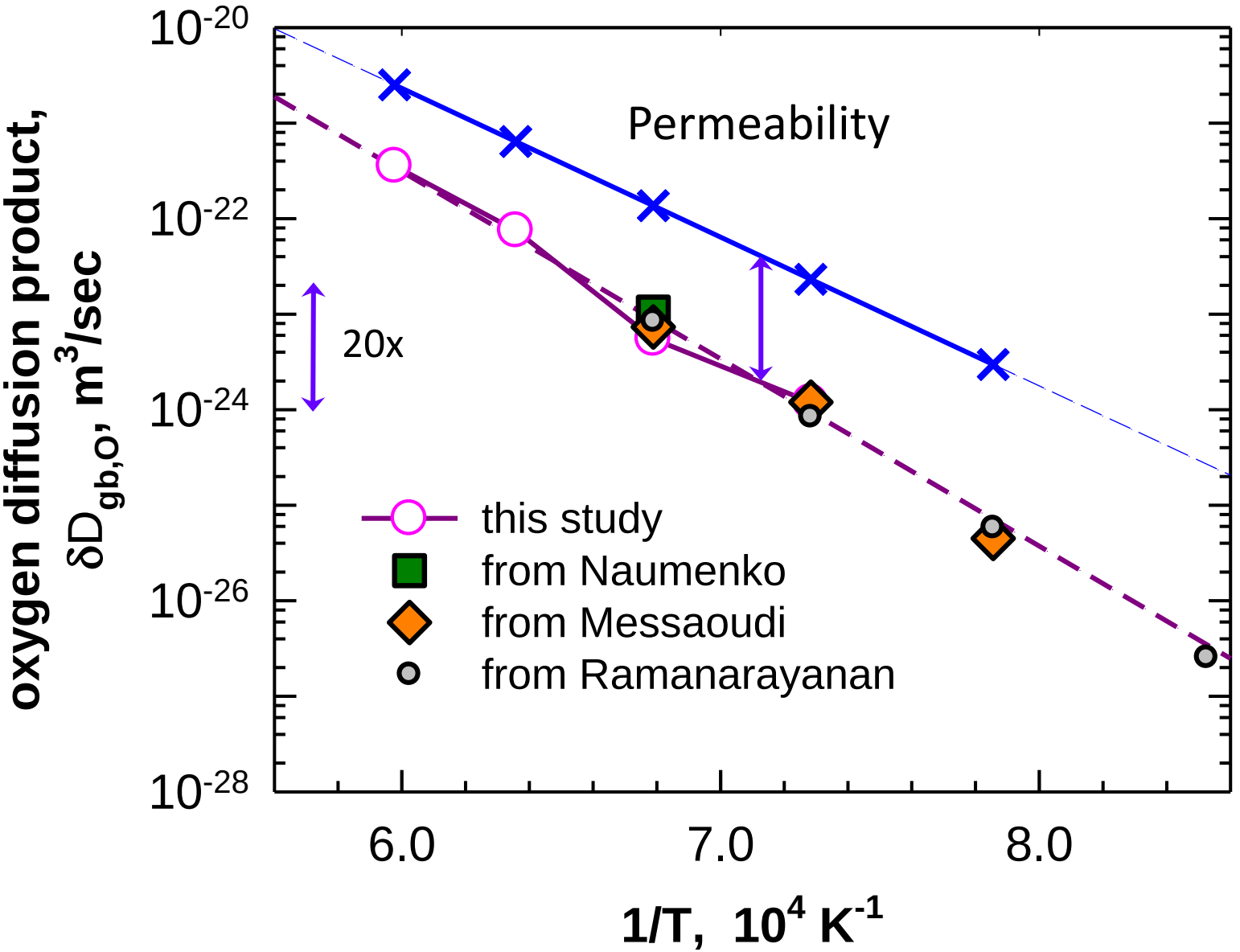
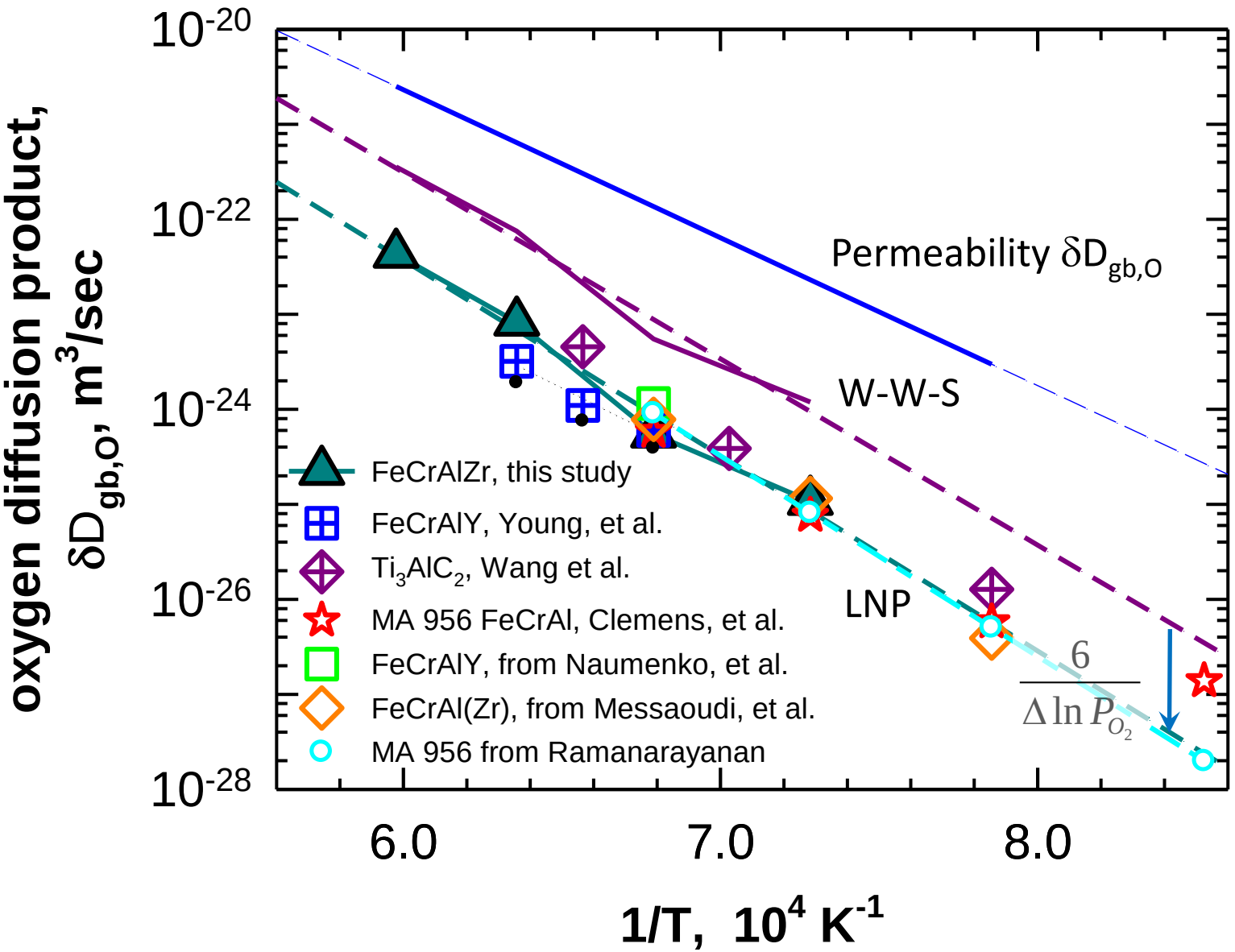
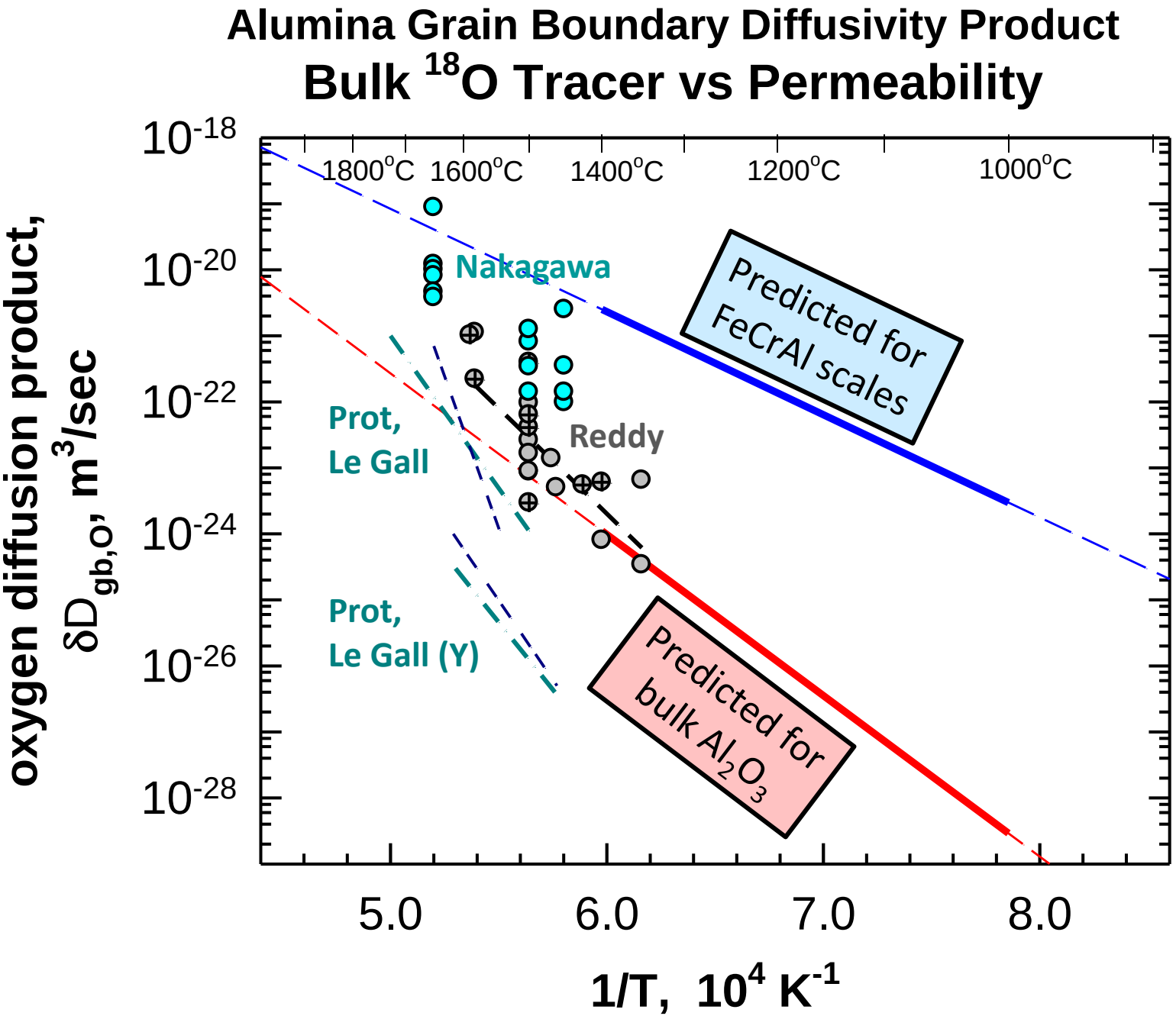
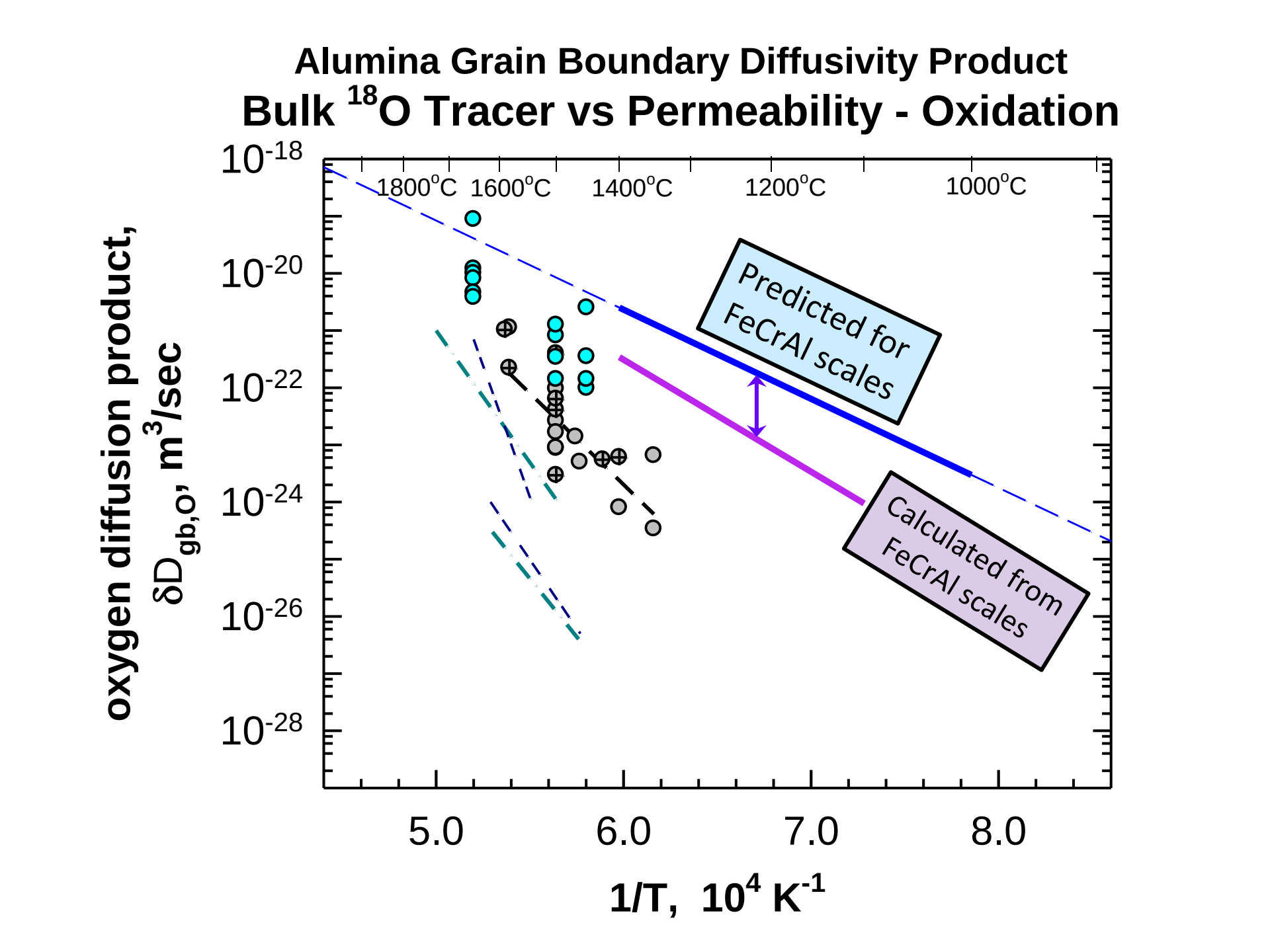


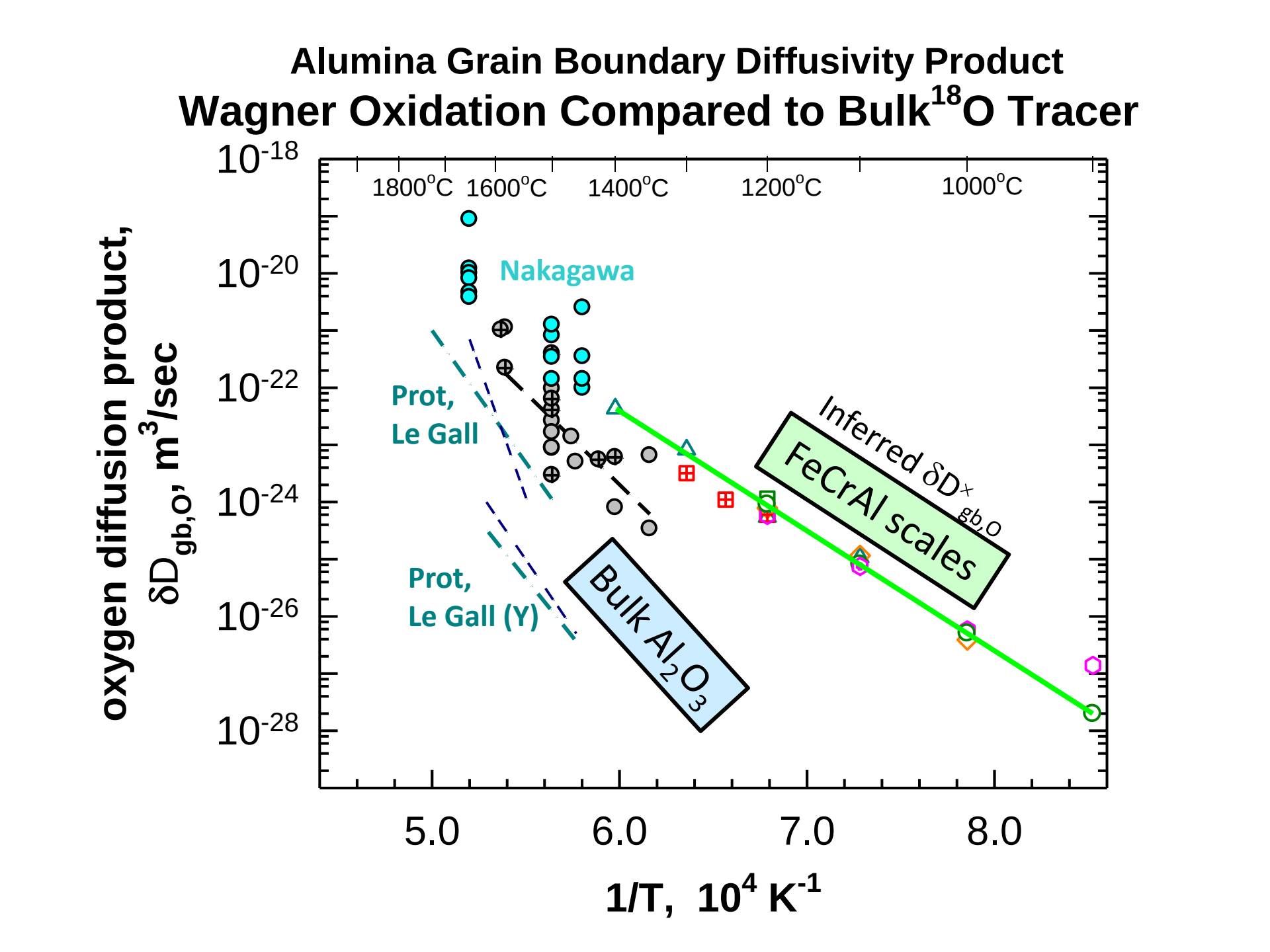
Scale Grain Boundary Diffusivity Product, $\Delta \ln P_{O2}$ solution

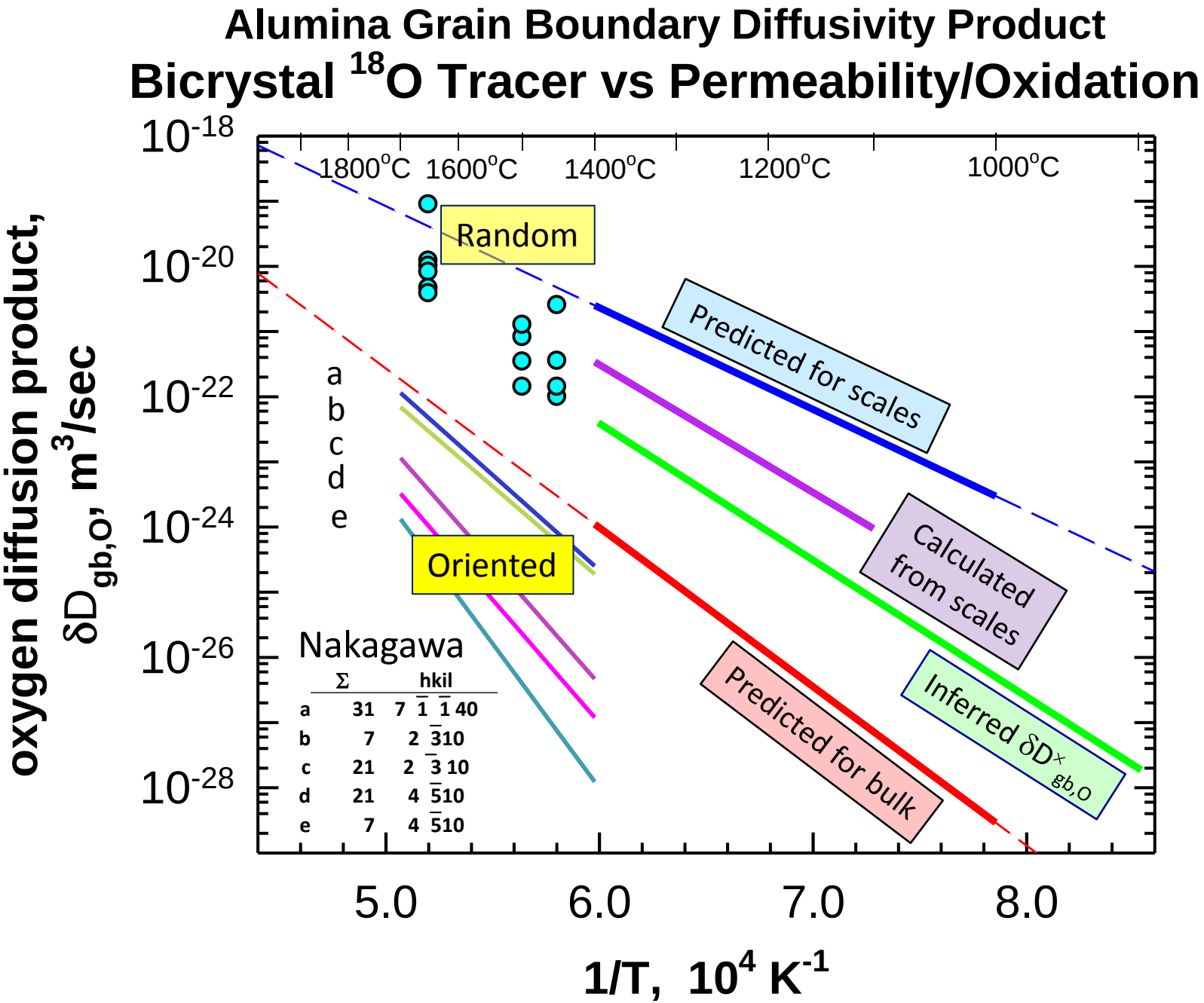
$\delta D_{gb,O}$ from Oxidation (FeCrAl(X), Ti_3AlC_2)




Alumina Grain Boundary Diffusivity Product
Bulk ^{18}O Tracer vs Permeability
oxygen diffusion product, $\delta D_{gb,O}$, m^3/sec
10^{-18}
10^{-20}
10^{-22}
10^{-24}
10^{-26}
10^{-28}
1800°C
1600°C
1400°C
1200°C
1000°C
Nakagawa
Predicted for FeCrAl scales
Prot, Le Gall
Reddy
Prot, Le Gall (Y)
Predicted for bulk Al_2O_3
5.0
6.0
7.0
8.0
1/T, 10^4 K^{-1}


Alumina Grain Boundary Diffusivity Product
Bulk 18O Tracer vs Permeability - Oxidation
oxygen diffusion product, δDgb,O, m3/sec
10-18
10-20
10-22
10-24
10-26
10-28
1800°C
1600°C
1400°C
1200°C
1000°C
Predicted for FeCrAl scales
Calculated from FeCrAl scales
5.0
6.0
7.0
8.0
1/T, 10^4 K^-1


Alumina Grain Boundary Diffusivity Product
Wagner Oxidation Compared to Bulk 18O Tracer
oxygen diffusion product, δD gb,O, m3/sec
10-18
10-20
10-22
10-24
10-26
10-28
1800°C
1600°C
1400°C
1200°C
1000°C
Nakagawa
Prot, Le Gall
Prot, Le Gall (Y)
Bulk Al2O3
Inferred δDx gb,O
FeCrAl scales
5.0
6.0
7.0
8.0
1/T, 10^4 K^-1


Alumina Grain Boundary Diffusivity Product
Bicrystal 18O Tracer vs Permeability/Oxidation
oxygen diffusion product, δDgb,O, m3/sec
10-18
10-20
10-22
10-24
10-26
10-28
1800°C
1600°C
1400°C
1200°C
1000°C
Random
Predicted for scales
Calculated from scales
Inferred δDx gb,O
Predicted for bulk
Oriented
a
b
c
d
e
Nakagawa
Σ hkil
a 31 7 1̄ 1̄ 40
b 7 2 3̄10
c 21 2 3̄ 10
d 21 4 5̄10
e 7 4 5̄10
5.0
6.0
7.0
8.0
1/T, 10^4 K^-1

Dopant Effects from Permeability Analyses

Matsudaira, Wada, Saitoh, Kitaoka

- Lu reduces δD_{gb} (oxygen) by 5x
- Hf reduces δD_{gb} (aluminum) by 3x
- Lu + Hf increase δD_{gb} (Al and oxygen) by 2x

Alumina Scale Growth Mechanisms:
Some New Attractions from Permeability Analyses

Bulk values (1 atm) should not agree with scale values (10^{-33}-10^{-23} atm):

Predicts $\delta D_{gb,O,\ scales} \approx 10^{4}\ \delta D_{gb,O,\ bulk}$

Alumina Scale Growth Mechanisms:
Some New Attractions from Permeability Analyses

- Bulk δD_{gb} should **not** agree with scale; $\delta D_{gb,O,\ scales} \approx 10^4\ \delta D_{gb,O,\ bulk}$

- **Interface (Oxygen): $\delta D_{gb,O}$ and $[V_O^{\circ\circ}] \propto (p_{O2})^{-1/6}$**
- **Gas surface (Aluminum): $\delta D_{gb,Al,}$ and $[V_{Al}^{\prime\prime\prime}] \propto (p_{O2})^{+3/16}$**
- **$\delta D_{gb,O} >> \delta D_{gb,Al}$**

Alumina Scale Growth Mechanisms:
Some New Attractions from Permeability Analyses

- Bulk δD_{gb} should **not** agree with scale; $\delta D_{gb,O,\ scales} \approx 10^4\ \delta D_{gb,O,\ bulk}$
- Interface $\delta D_{gb,O,}\ [V_O^{\circ\circ}] \propto p(O_{O2})^{-1/6}$; Gas surface $\delta D_{gb,Al,}\ [V_{Al}^{\circ\circ}] \propto p(O_{O2})^{+3/16}$

Oxidation Constant, Π, Gives Oxygen Diffusivity:

$$\Pi_i = k_{p,i} \cdot G_i = 12\ \delta D_{gb,O}$$

(and vice versa)

Alumina Scale Growth Mechanisms:
Some New Attractions from Permeability Analyses

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- $\Pi_I = k_{p,i} \cdot G_i = 12\ \delta D_{gb,O}$

$$\mathbf{Q_{interface} = Q_{1\ atm} + 1/n\ Q_{P(equilibrium)}}$$

298 = 467 - 1/6 (1012) kJ/mole

375 = measured from scales

Alumina Scale Growth Mechanisms:
Some New Attractions from Permeability Analyses

- Bulk δD_{gb} should **not** agree with scale; $\delta D_{gb,O,\ scales} \approx 10^4\ \delta D_{gb,O,\ bulk}$
- Interface $\delta D_{gb,O,}\ [V_O^{\circ\circ}] \propto p(O_{O2})^{-1/6}$; Gas surface $\delta D_{gb,Al,}\ [V_{Al}^{\circ\circ}] \propto p(O_{O2})^{+3/16}$
- $\Pi_I = k_{p,i} \cdot G_i = 12\ \delta D_{gb,O}$
- 298 kJ/mole predicted for scales; 375 kJ/mole measured for scales

Highly Variable $\delta D_{gb,O}$ Bulk ^{18}O Measurements

(Tsubasa Nakagawa, et al., U. Tokyo; CWRU)

$\delta D_{gb,O}$ (random) up to 10^8 $\delta D_{gb,O}$ (bicrystal)

$\Sigma 7$, $(45\bar{1}0)$ hkil

Alumina Scale Growth Mechanisms:
Some New Attractions from Permeability Analyses

- Bulk δD_{gb} should **not** agree with scale; $\delta D_{gb,O,\ scales} \approx 10^4\ \delta D_{gb,O,\ bulk}$
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- $\Pi_I = k_{p,i} \cdot G_i = 12\ \delta D_{gb,O}$
- 298 kJ/mole predicted for scales; 375 kJ/mole measured for scales
- $\delta D_{gb,O}$ (random) = $10^8\ \delta D_{gb,O}$, $\Sigma 7$, $(4\bar{5}10)$ hkil bicrystal