Advancement in waste glass formulation methodology

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SumGlass, Nimes, France

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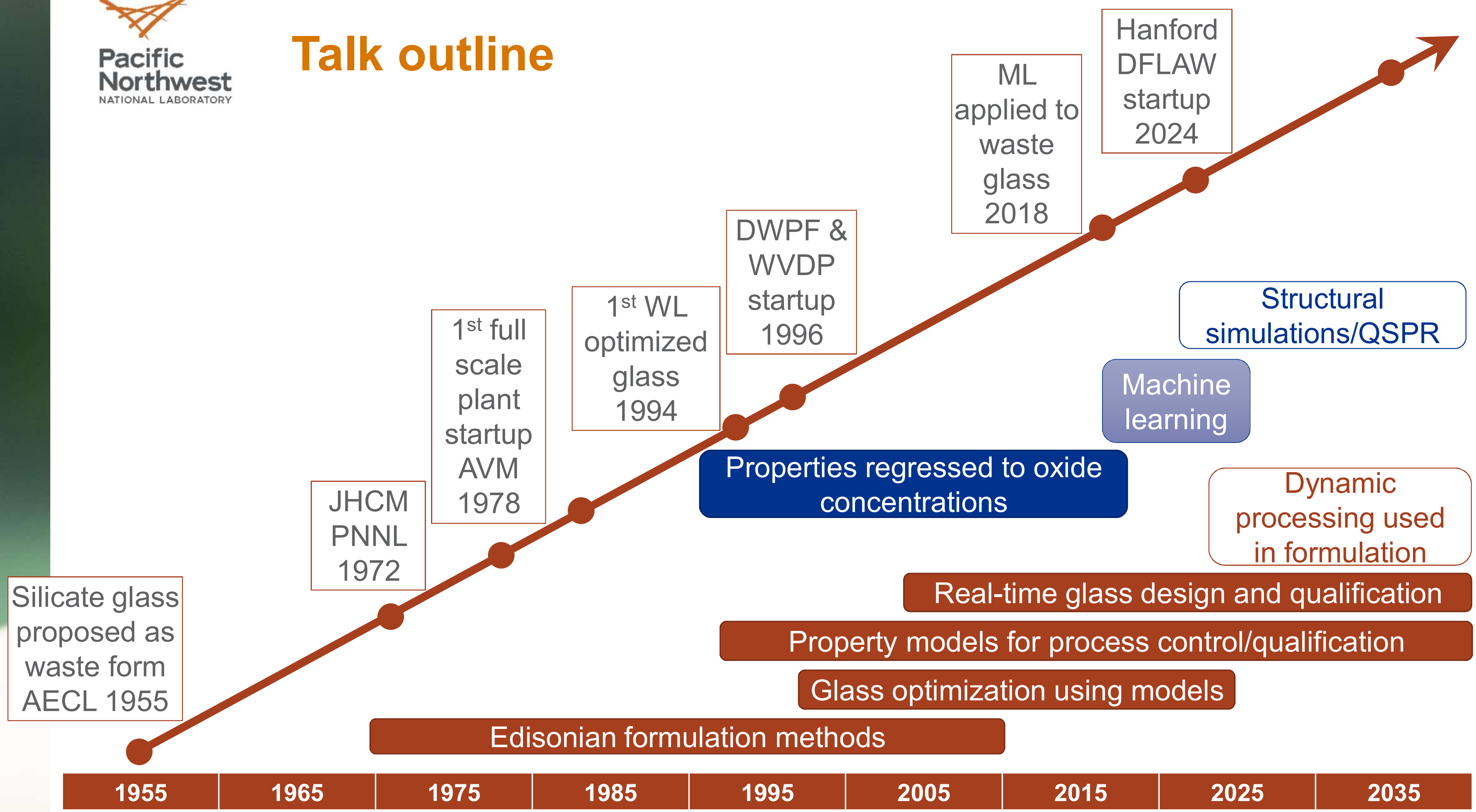
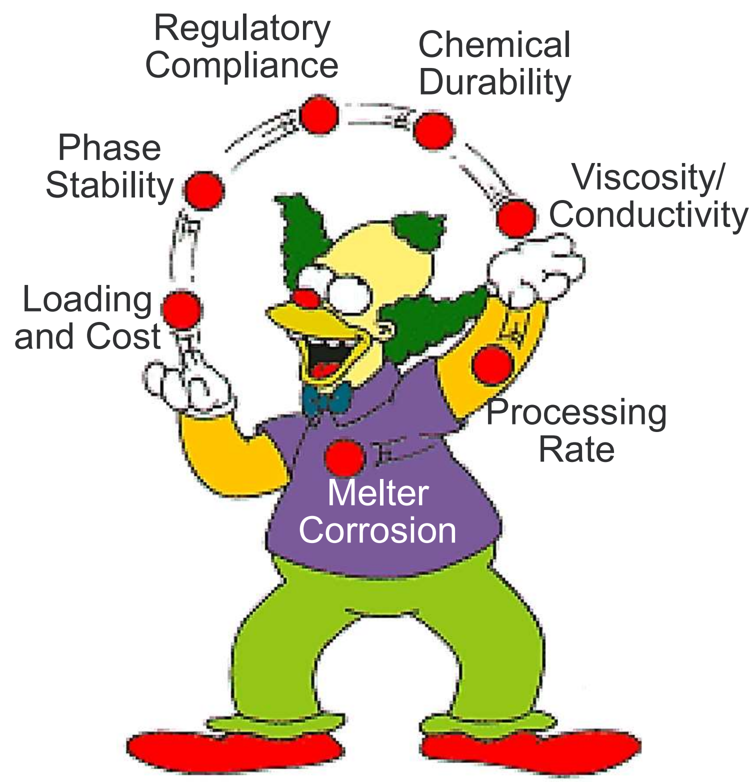
Talk outline



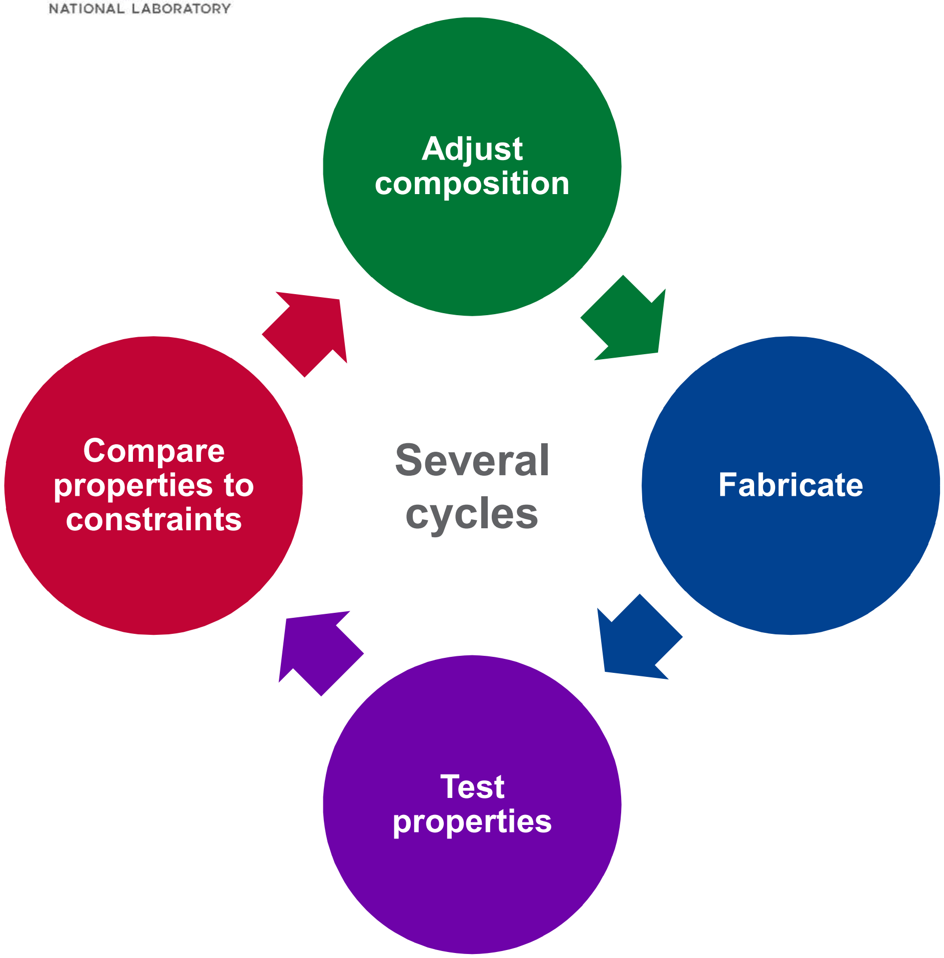
Waste glass formulation

- Each glass formulation must simultaneously satisfy a full set of requirements
  - Product quality
  - Processability
  - Cost efficiency



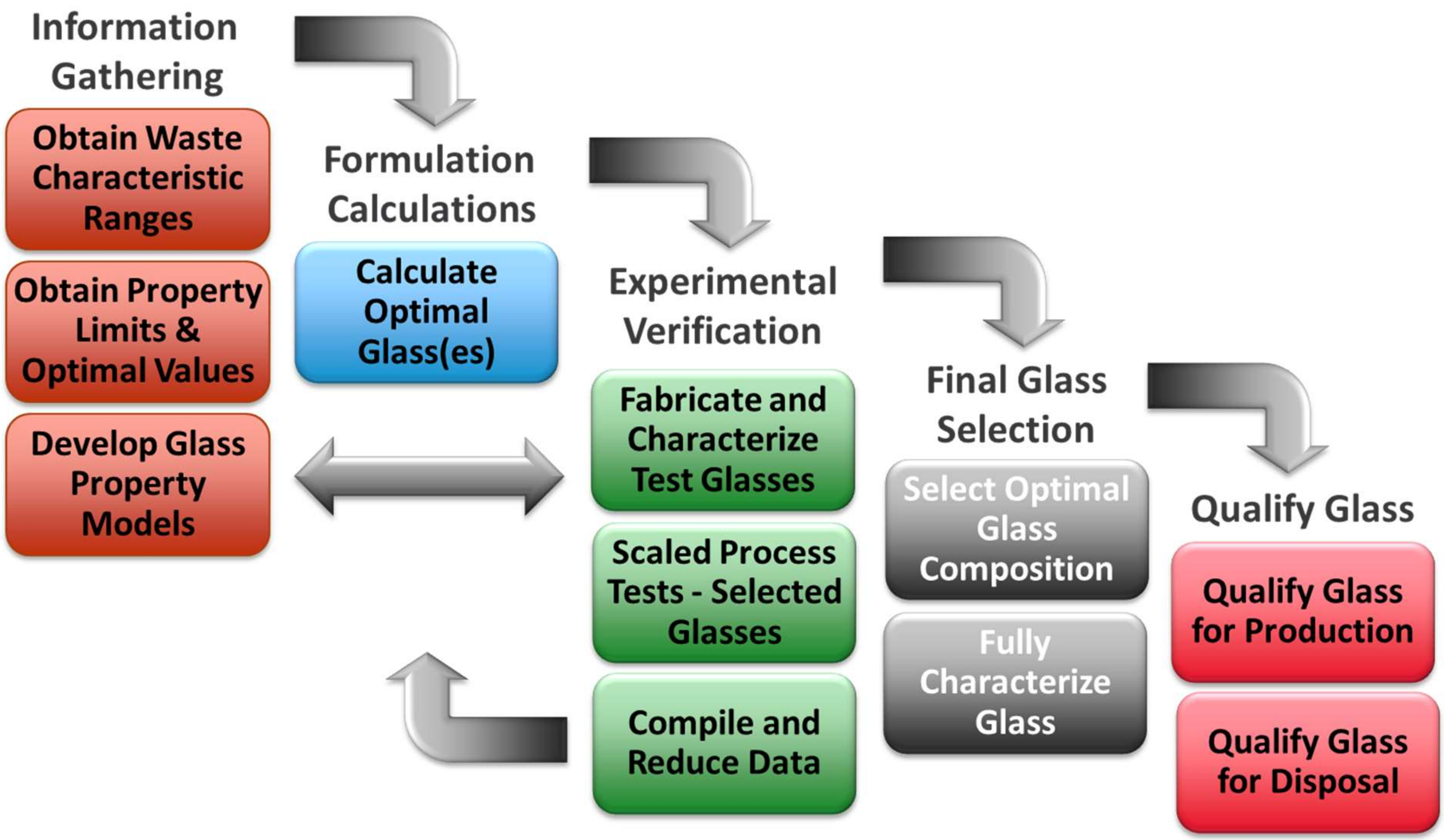
Vienna 2014, SumGlass 2013 Proceedings, *Proc. Matl. Sci*. **7**:148-155

Edisonian glass design



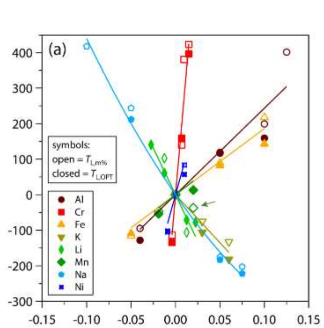
- Iterative glass formulation, testing, composition adjustment
- Time consuming (typically years)
- Can canvas likely composition variation with experiments
- Relatively low risk of glasses failing criteria, high risk of sub optimal solution
- Process has been successfully implemented for millennia

Typical glass formulation process with models



Experimental design methods

Increasing optimality

<table>
<tr><th>Design Type</th><th>OCAT</th><th>Factorial</th><th>Extreme vertices</th><th>Space-filling</th><th>Autonomous (GPR based)</th></tr>
<tr><td>Graphic</td>
<td>
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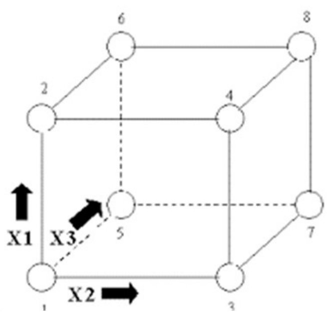
<td>
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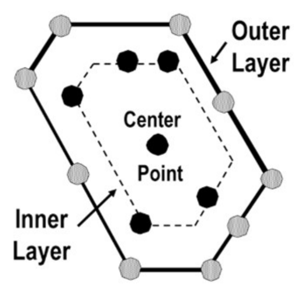
<td>
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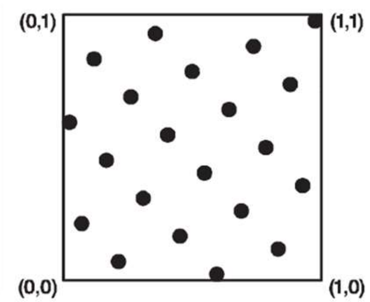
<td>
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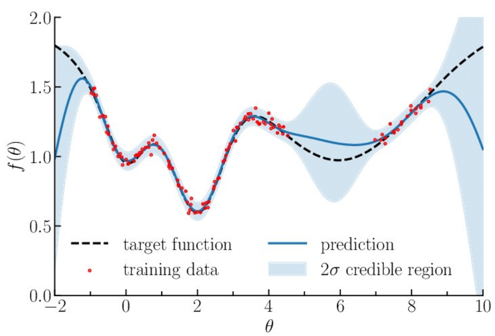
<td>
</td></tr>
<tr><td>Pros</td>
<td>Simple construction
Easy to visualize non-linear component effects</td>
<td>Simple construction
Estimates cross-term effects</td>
<td>Few points per variable
Some non-linear effects</td>
<td>Non-linear effects (single components and cross term)
Few extreme compositions</td>
<td>Non-parametric
Find compositional spaces with large uncertainty</td></tr>
<tr><td>Cons</td>
<td>No cross-term effects
Many points per variable</td>
<td>Many points per variable
Linear effects only
Extreme compositions</td>
<td>Challenging to construct extreme compositions</td>
<td>Challenging to construct</td>
<td>High computational costs</td></tr>
</table>

Lu, X, et al. 2023. *J. Am. Ceram. Soc.* DOI:10.1111/jace.19333

Experimental methods

Viscosity

ASTM C965

Conductivity

ASTM C657

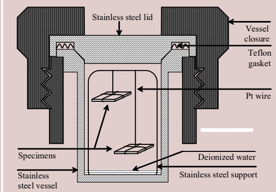
PCT

ASTM C1285

MCC-1

ASTM C1220

VHT



ASTM C1663

TCLP

SW846-1311

Liquidus

ASTM C1720

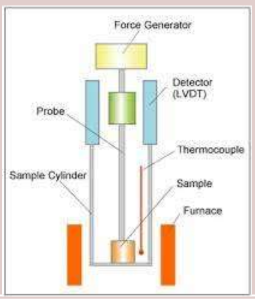
CCC-Crystal

ASTM C1720

Cp

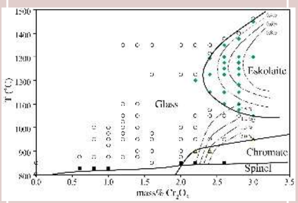
ASTM E1269

Tg



ASTM E1545

TTT



Grange 1941

Salt

Jin et al. 2018

Typical glass property models

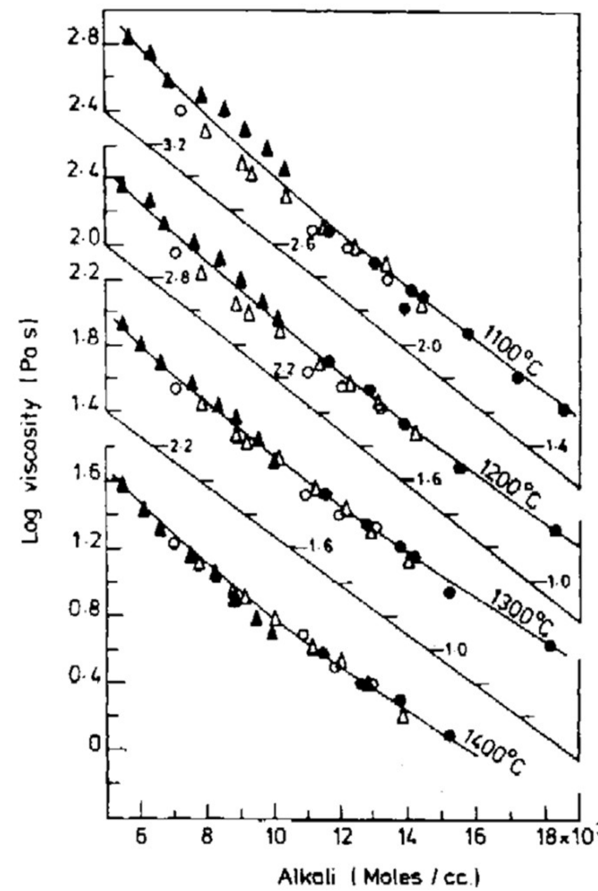
Partial quadratic mixture (**PQM**) model form:

$$f(P) = \sum_{i=1}^{q} p_i x_i + \text{ Selected } \left\{ \sum_{i=1}^{q} p_{ii} x_i^2 + \sum_{i\ <}^{q-1} \sum_{j}^{q} p_{ij} x_i x_j \right\} + e$$

P = property, p_i = i^{th} term coefficient, x_i = i^{th} term mass or mole fraction, p_{ii} = i^{th} quadratic term coefficient, p_{ij} = i^{th}-j^{th} cross product term coefficient

- Most property values vary smoothly with composition
- Some properties also vary with temperature (e.g., η, ε) for which common equations are used

Model	Equation
Arrhenius	$\ln(\eta) = A + \frac{B(\mathbf{x})}{T}$
Vogel-Fulcher-Tammann	$\ln(\eta) = A + \frac{B(\mathbf{x})}{T - T_0}$
MYEGA	$\ln(\eta) = A + \frac{B(\mathbf{x})}{T} exp\left(\frac{C}{T}\right)$



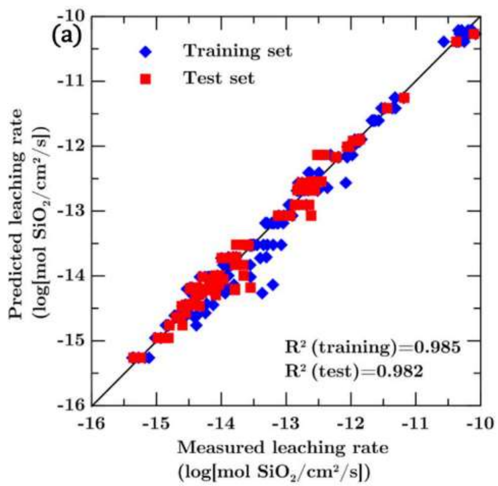
Vienna 2014, SumGlass 2013 Proceedings, *Proc. Matl. Sci*. **7**:148-155; Heredia-Langner et al. 2022, *IJAGS* 13:514-525

Property models with machine learning

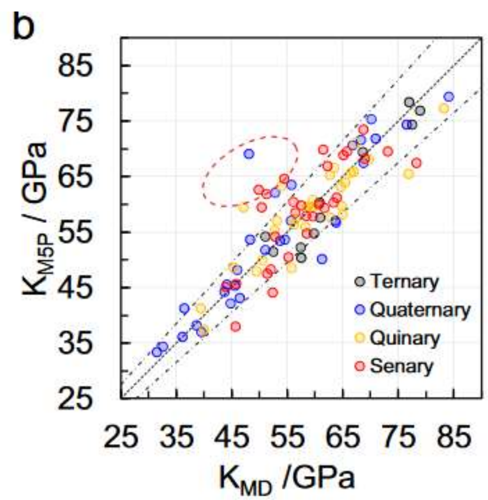
- Many methods developed to predict or categorize data using machine learning
  - E.g., LLR, GPR, ANN, SVM, KNN, DT, RF, GNB, QDA

Review articles:

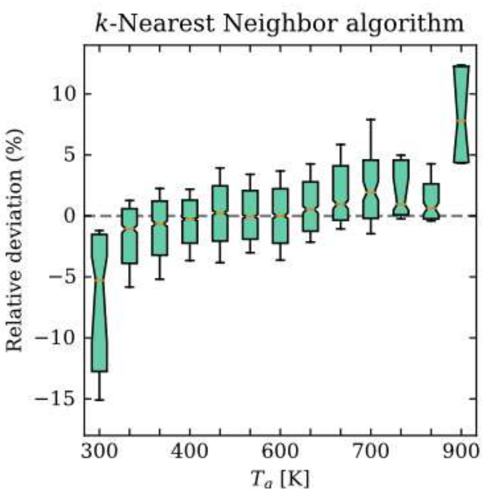
- De Guire et al. *J Am Ceram Soc.* 2019;102(11):6385–6406.
- Liu et al. *J Non-Cryst Sol. X*. 2019;4:100036.
- Montazerian et al. *Int Mater Rev*. 2020;65(5):297–321.
- Singh et al. *Mater Sci Eng B*. 2022;284:115858.
- Lu et al. *J Am Ceram Soc*. 2023:19333



Dissolution [Krishnan et al. 2018]



Elastic Modulus [Hu et al. 2020]



Tg [Mastelini et al. 2022]

GlassNet

- Discussion of ML wouldn't be complete without mentioning Cassar's GlassNet
  - An incredible tool that predicts many of the properties important to waste glasses
  - However, it doesn't predict all properties of interest, and isn't currently available under the needed QA

GlassNet: a multitask deep neural network for predicting many glass properties

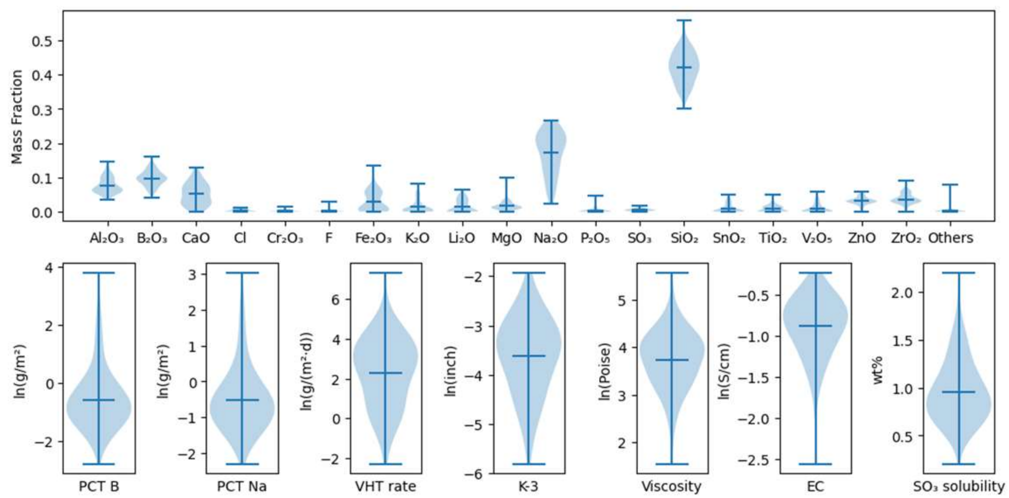
Daniel R. Cassar

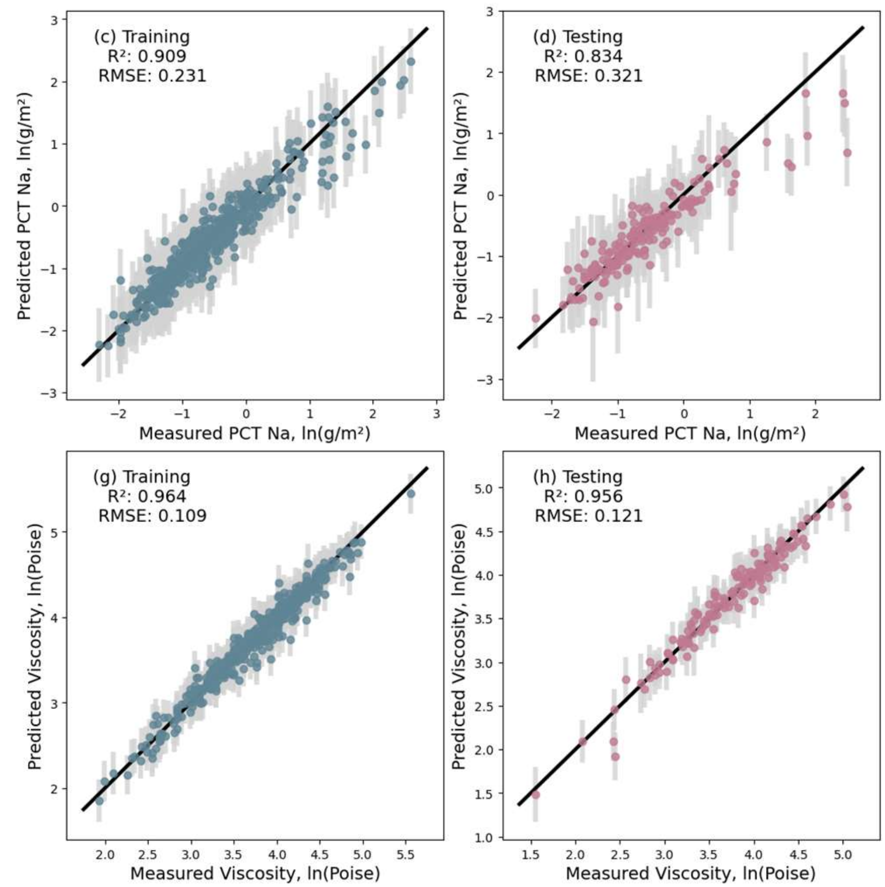
Ilum School of Science, Brazilian Center for Research in Energy and Materials (CNPEM), Zip Code 13083-970, Campinas, Sao Paulo, Brazil.
daniel.cassar@ilum.cnpem.br

Property	Minimum	Maximum
T_3	–	2350
T_4	–	2000
$\log_{10}(\eta(1773\,\mathrm{K}))$	–	10
$\log_{10}(\eta(1873\,\mathrm{K}))$	–	10
$\log_{10}(\eta(2073\,\mathrm{K}))$	–	8
$\log_{10}(\eta(2273\,\mathrm{K}))$	–	8
T_{soft}	–	1600
V_D	–	115
n_D	–	4
n (high)	1.7	3.5
ε	–	50
$\log_{10}(\tan(\delta))$	-4	-0.796
$T_{\rho=10^6\,\Omega.m}$	–	2000
$\log_{10}(\rho(273\,\mathrm{K}))$	–	40
$\log_{10}(\rho(373\,\mathrm{K}))$	–	28
$\log_{10}(\rho(1073\,\mathrm{K}))$	–	4
$\log_{10}(\rho(1273\,\mathrm{K}))$	–	5
E	–	175
H	–	15
ν	–	1
$D(293\,\mathrm{K})$	1	10
κ	–	6
$\log_{10}(\alpha_L(328\,\mathrm{K}))$	-6.5	–
$\log_{10}(\alpha_L(373\,\mathrm{K}))$	-6.5	–
$\log_{10}(\alpha_L(433\,\mathrm{K}))$	-8	–
$\log_{10}(\alpha_L(483\,\mathrm{K}))$	-7	–
$C_p(293\,\mathrm{K})$	–	2000
$C_p(473\,\mathrm{K})$	–	2000
$C_p(673\,\mathrm{K})$	–	3000
$C_p(1073\,\mathrm{K})$	500	2500
$C_p(1273\,\mathrm{K})$	500	3000
$C_p(1473\,\mathrm{K})$	500	3000
$C_p(1673\,\mathrm{K})$	500	2250
$\log_{10}(U_{max})$	-10	–
$\gamma(T > T_g)$	–	0.8
$\gamma(1473\,\mathrm{K})$	–	0.5
$\gamma(1573\,\mathrm{K})$	–	0.7

Waste glass optimization with ML models

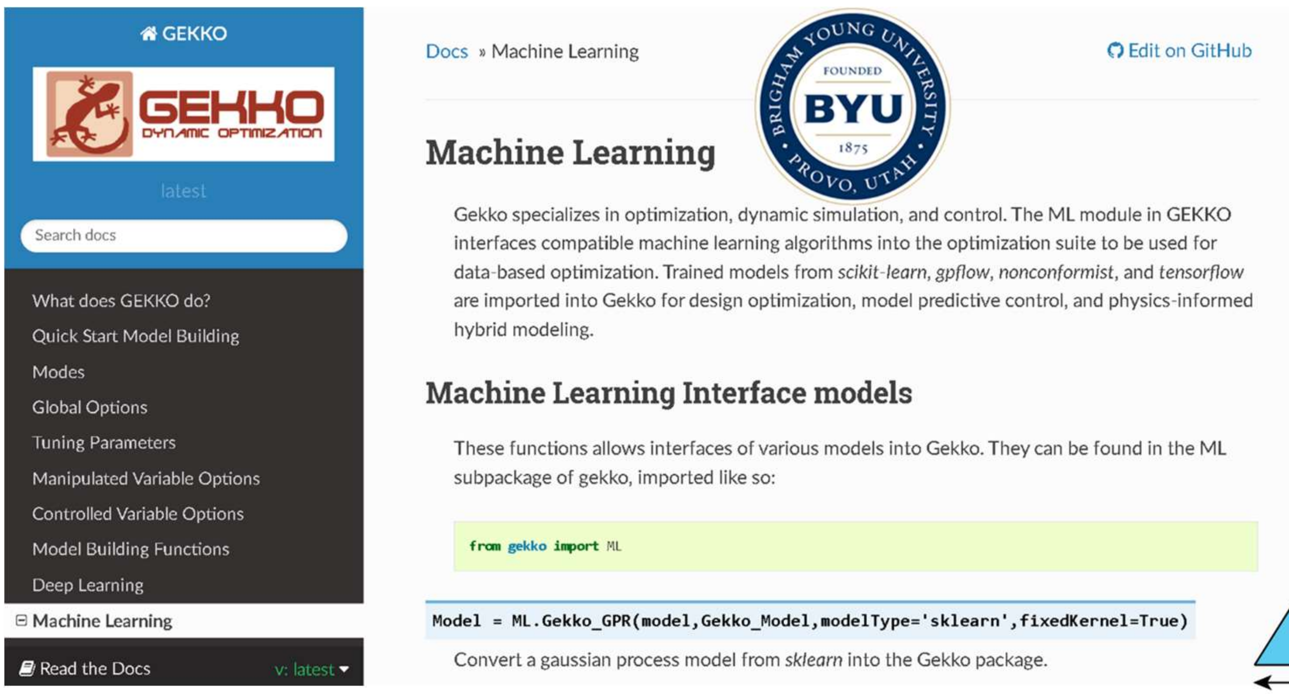
- Use mass fraction of glass oxide components for features to train models





Waste glass optimization with ML models

- Incorporated ML (sklearn) directly into optimization code (Gekko) [Gunnell et al.2023, Processes]
- Cannot directly handle uncertainties [Marcial et al. 2023, J Haz Mat.]
- Currently developing an analytical solution for process uncertainties



GEKKO

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Machine Learning

Gekko specializes in optimization, dynamic simulation, and control. The ML module in GEKKO interfaces compatible machine learning algorithms into the optimization suite to be used for data-based optimization. Trained models from *scikit-learn*, *gpflow*, *nonconformist*, and *tensorflow* are imported into Gekko for design optimization, model predictive control, and physics-informed hybrid modeling.

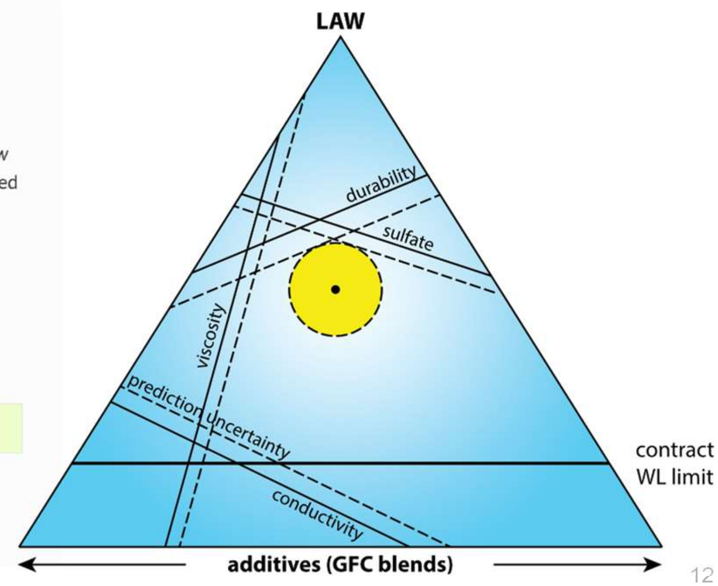
Machine Learning Interface models

These functions allows interfaces of various models into Gekko. They can be found in the ML subpackage of gekko, imported like so:

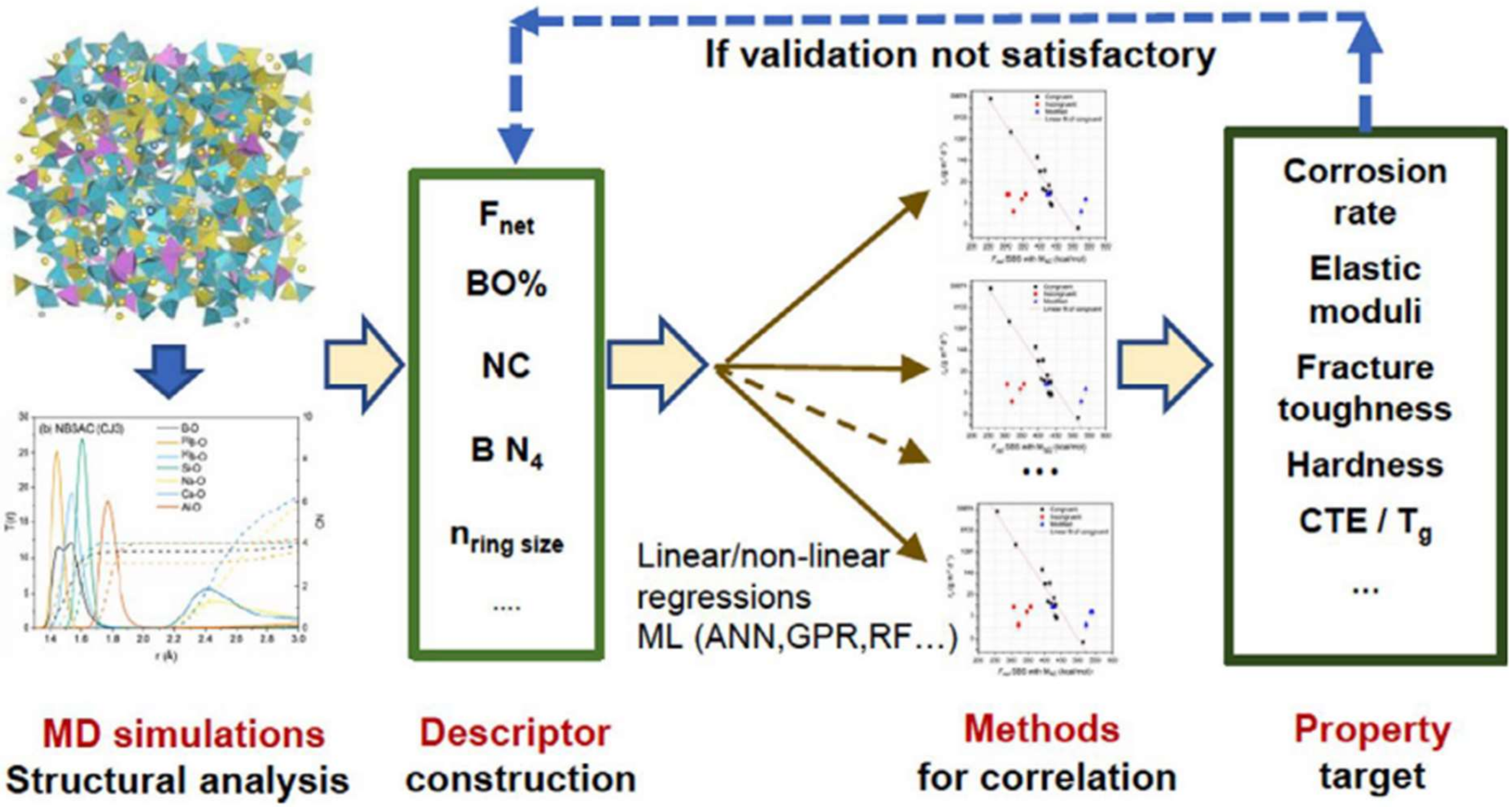
```
from gekko import ML
```

```
Model = ML.Gekko_GPR(model,Gekko_Model,modelType='sklearn',fixedKernel=True)
```

Convert a gaussian process model from *sklearn* into the Gekko package.



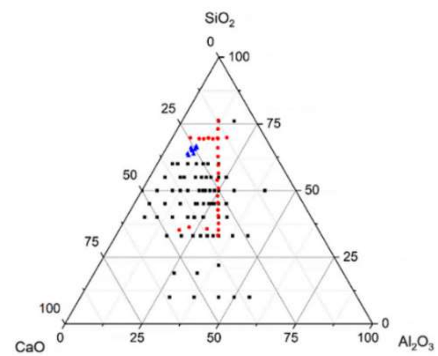
Quantitative structure-property relationship (QSPR)



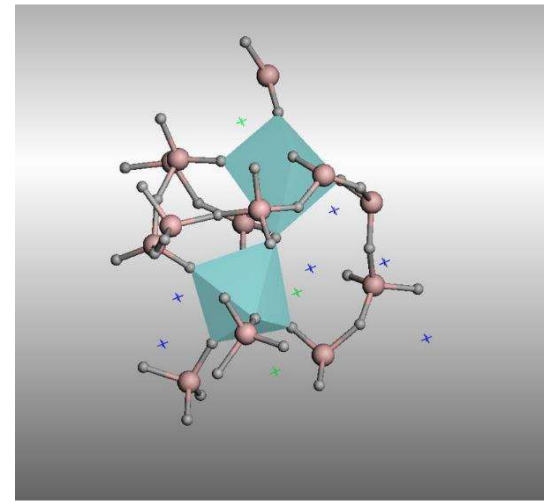
Du et al. 2021. *J. Am. Ceram. Soc*, **104**(9):4445-4458.

Model terms/features

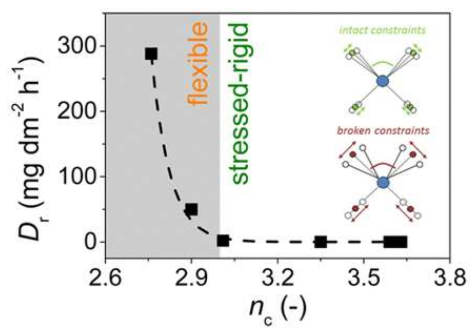
- ❑ Compositions
- ❑ Structural features/descriptors
  - ○ Theoretical calculations
    - Boron coordination (N_4)
    - Non bridging oxygen (NBO)
    - Network connectivity
  - ○ Experimental characterizations
    - NMR
    - XANES and EXAFS
    - Neutron diffraction/scattering
  - ○ Molecular dynamics (MD) simulations
  - ○ Topological constraint theory (TCT)
  - ○ QSPR (F_{net})
- ❑ Experimental conditions
  - Thermal history
  - Pressure
  - pH and temperature



Compositions

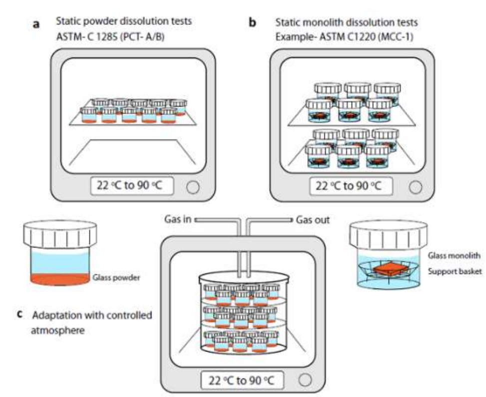


Structure features



Topological constraints

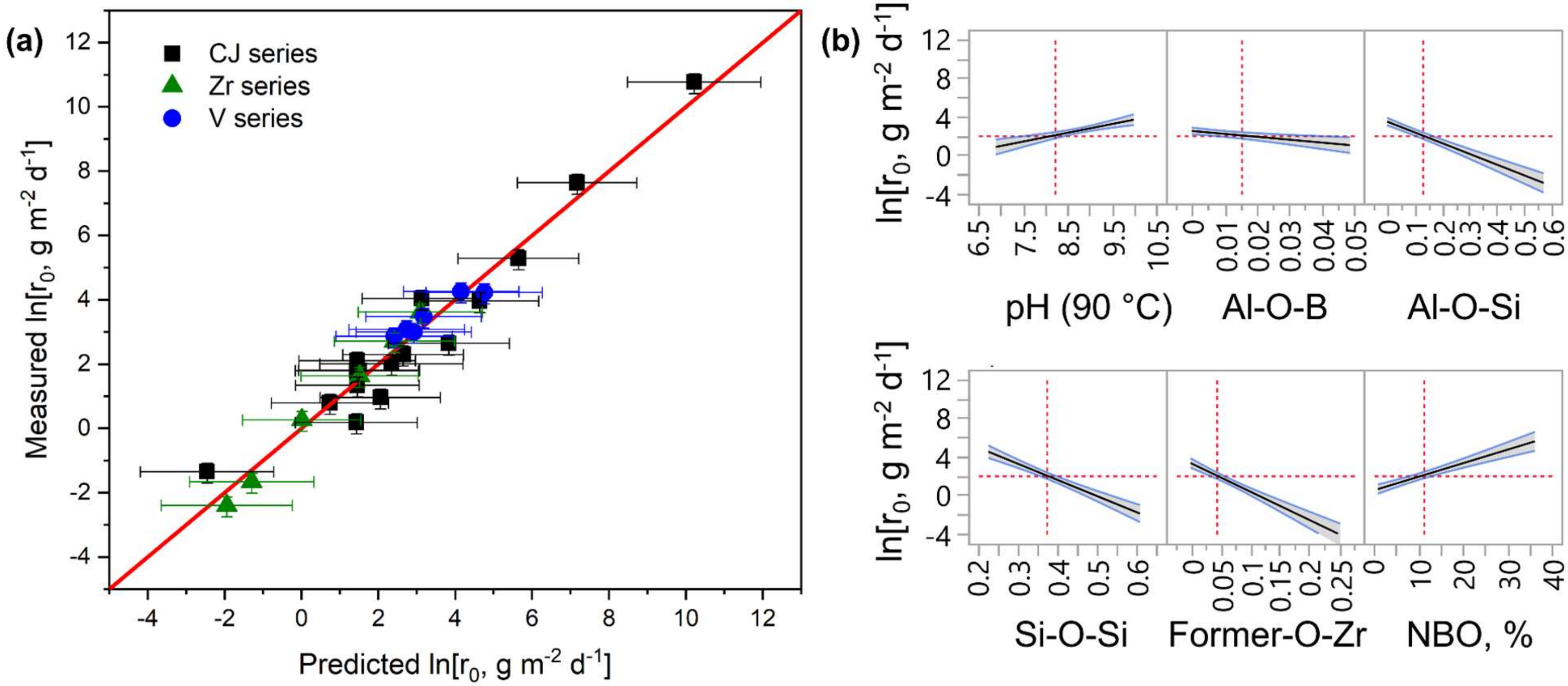
[Mascaraque et al. 2017]



Experimental conditions

[Thorpe et al. 2021]

Initial dissolution rate models with MD structural features



Lu et al. 2023. *J Am Ceram Soc.* **106**:1025-1036

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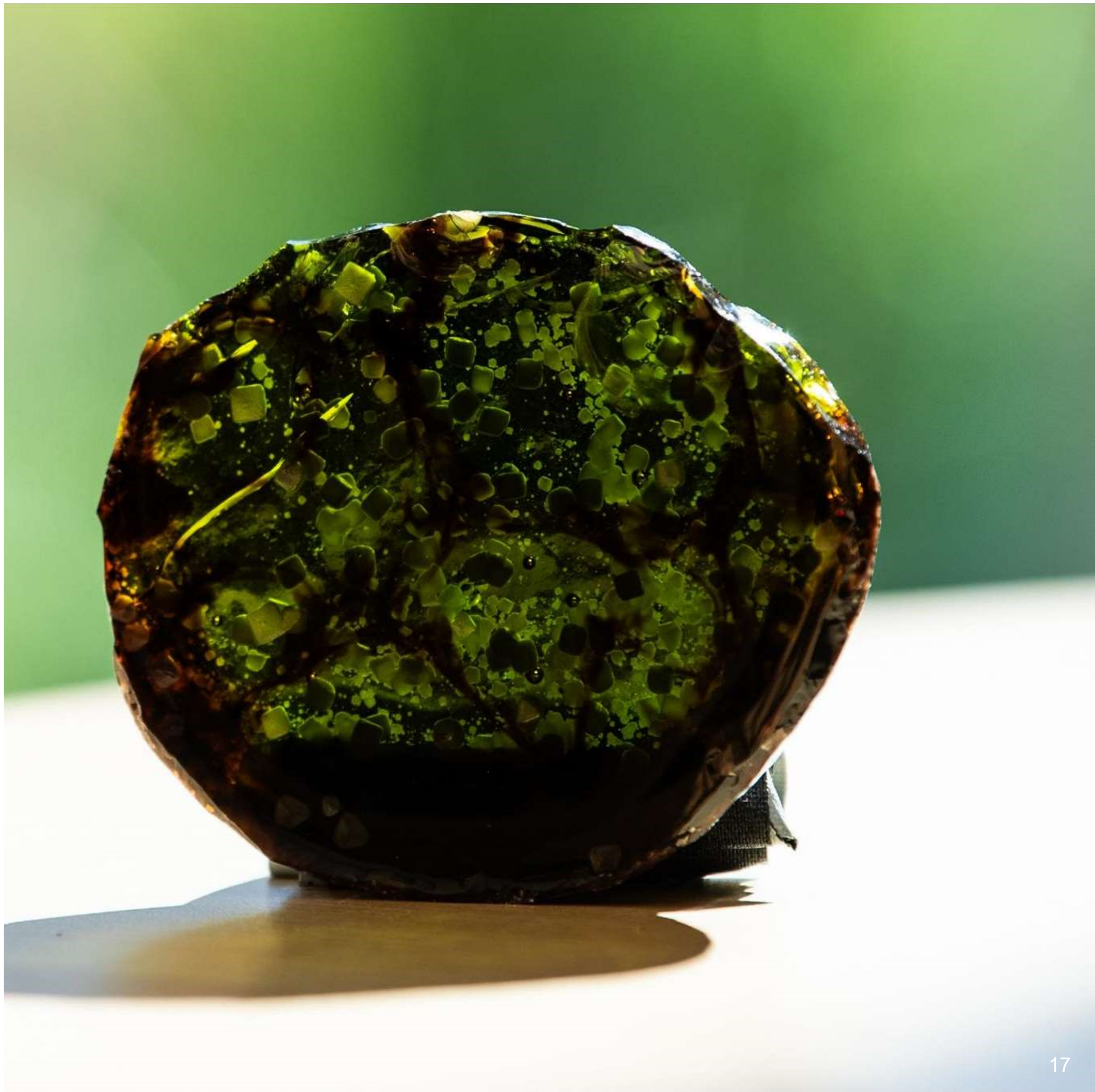
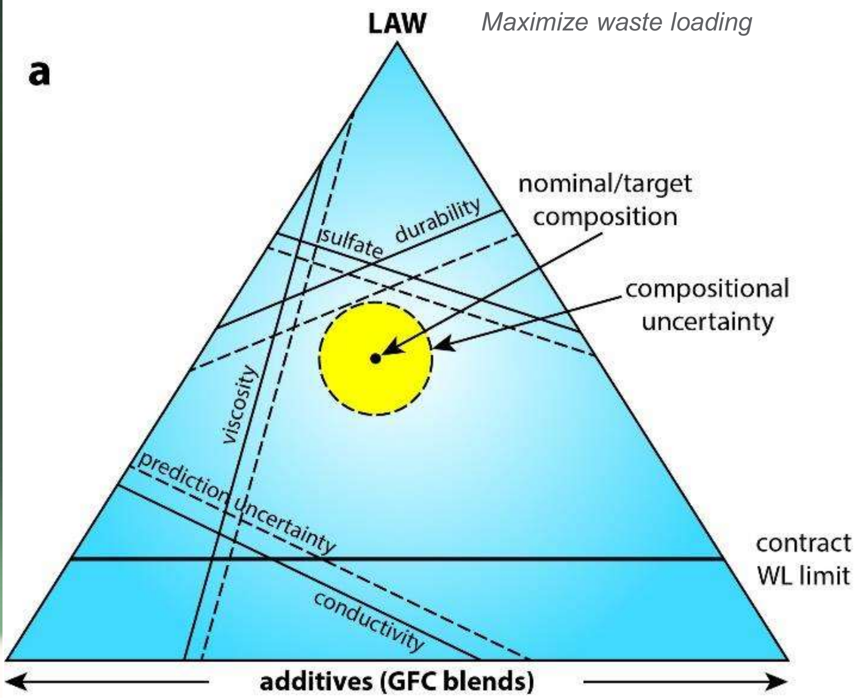
- We greatly appreciate financial support from the Department of Energy Office of River Protection, Waste Treatment Plant Project. With special thanks to Dr. Albert Kruger for support and technical oversight.
- We are also indebted to many colleagues who have helped bring the glass optimization process forward including those from UNT, WSU, SRNL, CUA, VNS, CEA, SHU, SU, BYU, CRIEPI, Rutgers, Alfred, and NNL.
- Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle Memorial Institute under contract DE-AC05-76RL01830.

Thank you



Nuclear waste glass optimization



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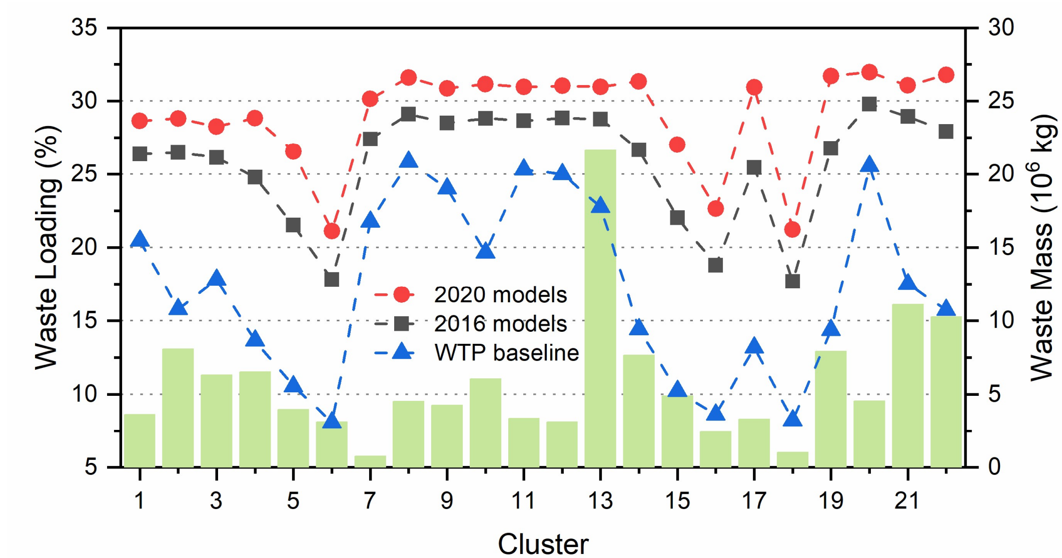
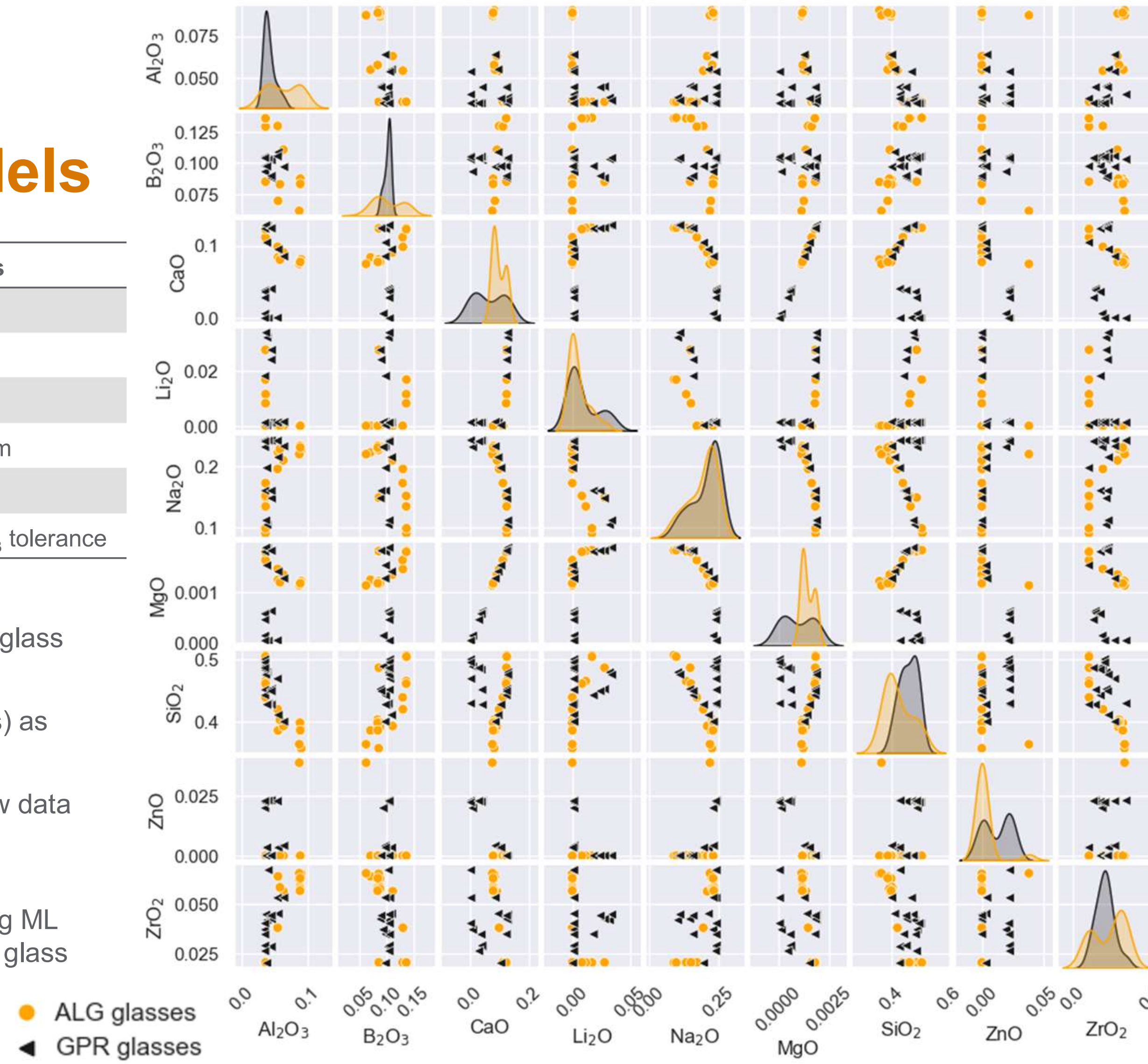


Marcial et al. (2023). *J Haz Matl*. 132437
Lu et al. (2021). *Nucl Eng Des.*, *385*:111543.

Waste glass optimization with ML models

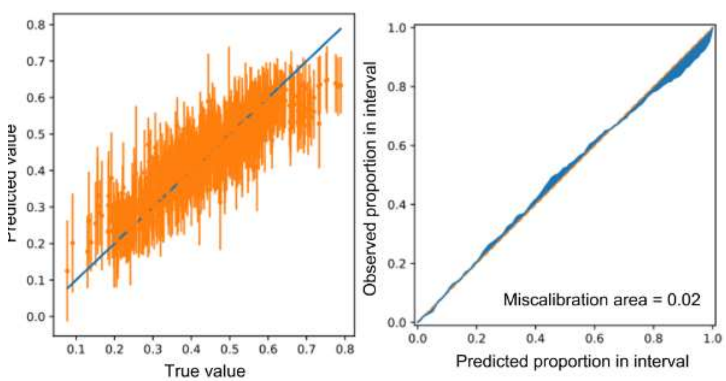
Property	Example Constraints
PCT-B	≤ 2 g/m^2
PCT-Na	≤ 2 g/m^2
VHT	≤ 50 g/m^2/d
ε_{1150}	0.12 ≤ ε_{1150} ≤ 0.59 S/cm
η_{1150}	20 ≤ η_{1150} ≤ 80 Poise
SO_3 tolerance (wt%)	SO_3 in melter feed ≤ melter SO_3 tolerance

- Developed a Python programing code to run glass optimization routine with the GPR models.
- Obtained comparable results (waste loadings) as using the traditional PQM property models.
- Glass optimization routine can learn from new data as generated, as well as update interpolation method conveniently.
- Be able to demonstrate the possibility of using ML models with prediction uncertainties in waste glass formulation.



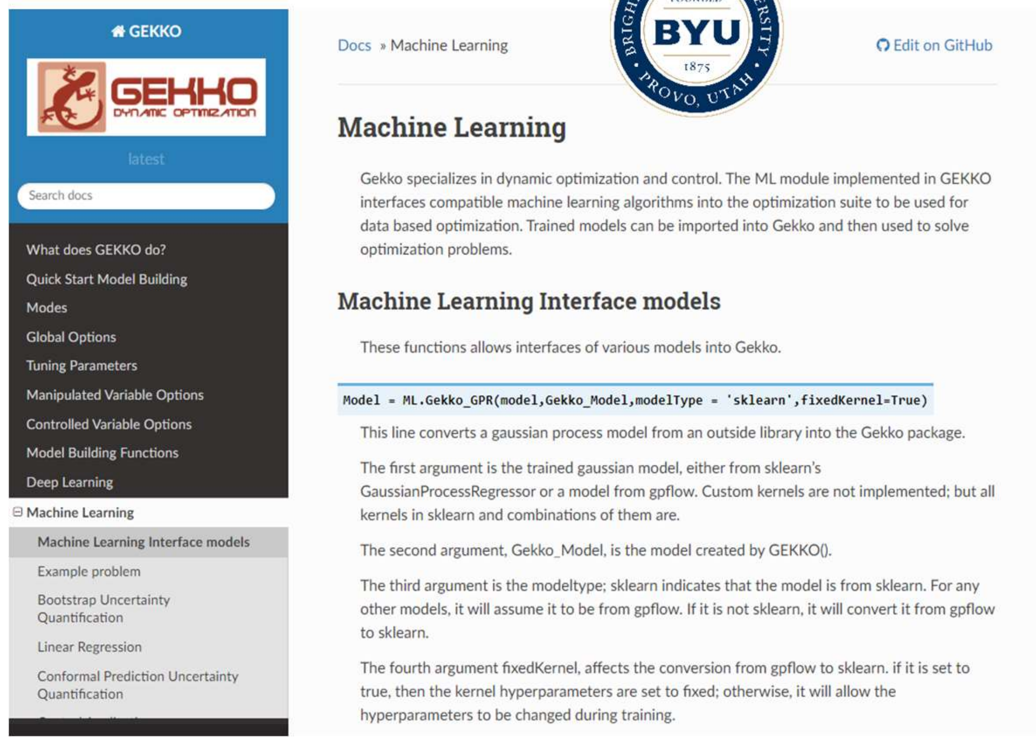
Challenges and outlook

- **Machine learning**
  - Standard protocols and benchmark models
  - Uncertainty quantification
  - Develop composition-structure-property models
- **Optimization**
  - Capacity issue of Python optimization packages with ML packages
  - Utilize HPC



(a) Gaussian Uncertainty

Gunnell et al. (2022). *Processes*, *10*(11), 2365.



Experimental validation of LAW ALG glasses