

MR. JARROD V. CRUM (Orcid ID : 0000-0001-9197-0878)

DR JOELLE T REISER (Orcid ID : 0000-0002-2638-1580)

DR BENJAMIN PARRUZOT (Orcid ID : 0000-0002-2841-6660)

Article type : Original Article

Seeded Stage III Glass Dissolution Behavior of a Statistically Designed Glass Matrix.

JV Crum, JT Reiser, BP Parruzot, JJ Neeway, JF Bonnett, SN Kerisit, SK Cooley, JV Ryan, GL Smith, and RM Asmussen

Pacific Northwest National Laboratory, Richland WA, USA

Abstract

The glass dissolution rate of some glasses accelerates after prolonged time spent at a slow, residual glass dissolution rate. This phenomenon is referred to as Stage III behavior. The acceleration in glass dissolution rate linked to Stage III behavior is significant and may be the most impactful to long-term performance of glass in a repository. This work is aimed at understanding the effect of glass composition on Stage III behavior to add a level of technical defensibility to glass disposal. To this end, a set of twenty-four glass compositions were statistically designed, where eight glass components (SiO_2 , B_2O_3 , Al_2O_3 , CaO , Na_2O , SnO_2 , ZrO_2 , and Others) have been independently varied in order to study the individual effects of each. These glasses have been subjected to static dissolution tests at 90 °C in deionized water and then seeded with zeolite Na-P2 28 days into the testing to induce Stage III behavior. The response of the glasses to the zeolite seeds fell into four primary types: 1) no response to seeds; 2) an immediate linear sustained acceleration in the rate; 3) an immediate linear

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1111/JACE.17823](https://doi.org/10.1111/JACE.17823)

This article is protected by copyright. All rights reserved

acceleration in the rate followed by a decrease; and, 4) a progressive acceleration in the rate that is concurrent with the addition of the seeds. The main glass components observed to influence these behaviors were CaO, Al₂O₃, B₂O₃, and ZrO₂, where: 1) CaO influenced which glasses showed a Stage III response to seeds (high CaO: Types 2, 3, and 4) or did not respond to seeds (low CaO: Type 1), 2) Al₂O₃ and B₂O₃ influenced which glasses showed a sustainable Stage III response (high Al₂O₃: Types 2 and 4) versus transitory response (low Al₂O₃ and high B₂O₃: Type 3), and 3) ZrO₂ concentration influenced whether glasses showed a linear (high ZrO₂: Type 2) versus progressive (low ZrO₂: Type 4) response to seeds.

1.0 Introduction

Countries around the world, including the United States (US), France, the United Kingdom (UK), Japan, China, and Russia, are developing or actively vitrifying high-level and low-activity (low-level, US only) radioactive waste and developing pathways for disposal of glass waste forms in a deep geologic repositories (for high-level waste, HLW) or near-surface disposal facilities (for low-activity waste, LAW). Regardless of the disposal location, acceptance for disposal requires a defensible safety case that uses models developed from experimental data that demonstrate how the glass waste forms corrode over time to obtain an estimate of contaminant and radionuclide release over geological time frames in the disposal environment ^[1].

The glass dissolution model should account for all three of the commonly discussed stages of glass corrosion: the initial rate (Stage I, fastest dissolution rate), the residual rate (Stage II, slowest dissolution rate) and a reacceleration rate (Stage III, to date shown to be in between Stage I and II dissolution rates) ^[2]. During Stage I, the glass experiences ion-exchange and congruent dissolution from a pristine glass surface^[1-3]. However, Stage I behavior is expected to be brief or non-existent in most disposal environments as the flow of groundwater is slow enough that the concentrations of glass constituents are either already present or will quickly increase in solution. Glass dissolution progressively slows with time and transitions to Stage II behavior. This slowing is explained by a series of changes to the glass surfaces and the solution. The pristine glass surface alters, forming a gel layer and secondary phases which may have passivating effects in some situations^[4,5]. Additionally, the elements released from the glass increase with time in solution, which leads to solution feedback effects that cause the glass dissolution rate to slow. The relative impacts of the alteration layer and the affinity effect are the subject of continued debate ^[3,6,7]. The slow residual rates of Stage II have been shown to occur for tens of years in static laboratory experiments ^[8-10]. The current data for Stage I and II glass dissolution are quite extensive ^[9,11-16] and are accounted for in models that estimate the long-term corrosion behavior of glass ^[17-24]. However, there is evidence that glasses demonstrating Stage II behavior can reaccelerate to Stage III glass dissolution behavior under certain conditions. Evaluation of the glass corrosion literature indicates that Stage III glass dissolution behavior generally occurs at elevated pH (≥ 10.5) and is linked to the formation of secondary phases that act like a sink for elements released from the glass ^[2,25-34]. In Stage III behavior, the sink phase unbalances the quasi-equilibrium established in Stage II and results in an increase in the glass dissolution rate. Stage III glass dissolution behavior can occur briefly or be sustained until the glass fully alters in laboratory experiments ^[3,27]. This work aims to determine correlations between composition and observed Stage III behavior that could be included in future glass dissolution models for

nuclear waste form disposal.

1.1 Background on Stage III Behavior

Stage III glass dissolution behavior has been attributed to the formation of zeolite secondary phases in long-term static dissolution experiments on borosilicate glasses [2,10,26,27,29,32,34-37]. Despite the agreement that Stage III behavior coincides with the formation of zeolitic phases, ongoing research continues to address questions regarding the experimental conditions and glass properties that initiate and sustain Stage III glass dissolution behavior [26-28,31,38]. One difficulty in predicting the impact of Stage III glass dissolution behavior is the onset time, which is highly unpredictable and currently impossible to predict. The irregular onset time of zeolite growth, which coincides with Stage III behavior, may be due to slow zeolite nucleation and growth kinetics at test temperatures (typically 90 °C). Additionally, the duration of Stage III behavior is unknown as Stage III may be sustained until all the glass corrodes or may be transient.

In terms of assessing the relative impact of Stage III dissolution rates on the release of radionuclides from the glass, previous experimental results show that seeded, or induced, Stage III glass dissolution rates are slower than Stage I, but faster than Stage II (long-term residual) rates for silicate glasses [2]. However, this observation is limited to a small number of glass compositions. The concern is that Stage III glass dissolution rates may be fast enough to release contaminants and radionuclides at a rate that may exceed regulatory standards for a disposal facility. Unlike Stage I, which occurs over a very short duration (on the order of hours or days in the disposal facility), Stage III glass dissolution could continue until all of the glass is consumed as seen in previous works [2,26,28,31,39].

1.2 Zeolite Crystalline Seeded Approach to Initiate Stage III Behavior

Zeolite crystalline phases are generally present when solids analysis is performed after nuclear waste glasses undergo Stage III glass dissolution behavior during static dissolution testing [32,35]. The onset of Stage III glass dissolution behavior may be linked to nucleation and crystal growth of the zeolite phases. These unpredictable kinetics cause difficulties when designing experiments to measure the Stage III glass dissolution rates in regard to determining when to remove solution aliquots. For this reason, seeding the static dissolution experiments with zeolite crystalline seeds is an attractive option to induce Stage III behavior in a predictable manner, i.e., circumvent the nucleation and crystal growth induction time. Though this method has been used for quite some time, the zeolite seeds tested did not always effectively trigger a Stage III response [40-42]. However, recently Fournier et al. [28] found that zeolite P2 seeds consistently induced Stage III behavior for ISG. Test results

showed that the seeds caused Stage III dissolution behavior based on the elevated glass dissolution rates in the seeded tests compared to the unseeded test at 90 °C [28]. A later seeding study by Parruzot et al. [27] showed that Stage III onset and rates were dependent on the type of zeolite selected. The authors added either analcime, chabazite, P1 type, or P2 type crystalline phases (i.e., same composition, different crystalline structures) into static dissolution reactor vessels containing AFCI (originally named CSLNTM-C-1.5) [43], SRL-202A [44], or SON68 [45] glass after 50 days of reaction at 90 °C. Most often, upon zeolite addition, an immediate response was observed: the rate accelerated and then slowed (SON68, SRL-202A) or Stage III behavior persisted (sustained rate, AFCI and LAWA76). In certain cases (SRL-202A at 90 °C), after the initial response to zeolite addition, a second sustained acceleration occurred. The authors also showed that a Stage III response was observed at room temperature, 30 °C, 40 °C and 70 °C [27,28].

Because of the unpredictable onset time of Stage III behavior, currently there is insufficient Stage III glass dissolution data to predict the impact of Stage III on the overall dissolution behavior of glass disposal environments. To address the lengthy and unpredictable durations required to observe Stage III glass dissolution behavior, researchers have begun to seed static dissolution experiments with zeolite crystals to drive the glass to Stage III behavior [2,26-28]. However, tests that have employed the zeolite seeding technique are limited to a narrow range of glass compositions. To address this knowledge gap, we have applied the zeolite seeding technique to a wide range of glass compositions by designing a 24-glass matrix in an effort to understand the impact of glass composition on Stage III behavior and dissolution rates at a test temperature of 90 °C.

1.3 Matrix Design

For this work, a 24-glass matrix was statistically designed using the space filling design option in JMP12® software (SAS: Cary, NC). Seven major components (Al_2O_3 , B_2O_3 , CaO , Na_2O , SiO_2 , SnO_2 , and ZrO_2 , see Table 1) were varied independently, while all remaining components were grouped into an eighth “Others” component (Table 2) that was also varied. The enhanced waste glass (EWG) composition space being developed for higher waste loadings at the Hanford Waste Treatment and Immobilization Plant (WTP) was used as the representative test case that was used to determine the composition space for these tests. [46] The matrix glasses are referred to as enhanced LAW (eLAW) glasses. As the glasses were designed to represent compositions projected to be produced from Hanford LAW at WTP they are expected to be high in sodium as a result of the high sodium Hanford LAW (Table 1). High-Na glasses are also found in other nuclear waste glass compositions such as French AVM glasses (Na_2O up to 18.8wt%) [47-49].

The components varied in this work were selected because they typically influence glass dissolution prior to Stage III behavior and/or are commonly found in the secondary corrosion products, such as zeolites that contain Al, Na, Ca, and Si [e.g., analcime ($\text{Na}_{16.32}\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot 16\text{H}_2\text{O}$), P1 ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$), P2 ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 6\text{H}_2\text{O}$), and gobbinsite ($\text{Na}_{2.5}\text{Ca}_{0.6}\text{K}_{2.1}\text{Al}_{6.2}\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$)]. These oxides (Al_2O_3 , Na_2O , CaO , and SiO_2) along with B_2O_3 , SnO_2 , and ZrO_2 are expected to impact the glass structure and corrosion behavior of LAW glasses based on their component effects in recent HLW and LAW 7-day product consistency test (PCT) and LAW vapor hydration test (VHT) models [50,51]. To gain an understanding of the influence of glass composition on Stage III behavior it is important to provide even statistical coverage over the composition space applicable to EWG while avoiding testing compositions that will be excluded by the EWG LAW vitrification facility processing models for reasons such as viscosity, sulfur solubility, and/or crystallinity. With the goal of this work to determine composition–parameter correlations between glass composition and Stage III rates, the eventual statistical analysis of the data set will require good statistical coverage of composition space with minimal component correlations.

The design was constrained using the individual and multi-component constraints used to develop EWG property models for operation of the LAW vitrification facility [50]. The “Others” composition was selected to mimic the EWG Phase 2 matrix design for Hanford LAW glass [46].

Next, a series of multi-component constraints, given in Table 3, were selected to trim portions of the composition space and avoid ILAW glass composition space that are not projected to be produced within the WTP using currently planned EWG processing models [50]. These four multi-component constraints, listed in Table 3, were selected as follows:

- 1) for **Sulfur solubility**, boundary #1 ($\text{Na}_2\text{O} + 0.66 \cdot \text{K}_2\text{O} \leq 0.2600$) was moved from 0.2400 up to 0.2600 mass fraction and boundary #2 ($\text{Na}_2\text{O} + 0.66 \cdot \text{K}_2\text{O} + 11.69 \cdot \text{SO}_3 \leq 0.3594$) was moved from 0.3394 up to 0.3594 mass fraction, to be forward looking, for future glass formulations with increased waste loading;
- 2) the **Crystallinity constraint** ($\text{ZrO}_2 + \text{SnO}_2 + \text{Al}_2\text{O}_3 \leq 0.1700$) was selected to help minimize crystallization of Sn and Zr containing phases which could lead to processing issues in the melt; and,
- 3) **Viscosity at 1150 °C** was constrained between $2 \leq \eta \leq 10$, Pa·s with the latest LAW glass viscosity model to avoid unmelttable glass composition space.

With 24 glass compositions, the design from JMP provides three glasses per independent variable which is assumed sufficient to support fitting of the individual component effects and limited non-linear effects. The resulting glass compositions in supplemental **Error! Reference source not found.** were selected by the software to provide even coverage of the EWG composition space. Figure 1 provides a scatter plot matrix showing the selected glass compositions within the compositional space. From this plot it was evident the design provided even coverage of composition space in two dimensions (component to component) instead of placing all compositions at exterior points to better support any non-linear response versus composition. Some portions of the scatter plot matrix show regions of 2-D space that were excluded by the multi-component constraints. For example, the Al_2O_3 versus SnO_2 plot shows that the upper Al_2O_3 and upper SnO_2 corner is not populated with glass compositions because of the crystallinity constraint. Other plots, Al_2O_3 - B_2O_3 and Al_2O_3 - SiO_2 , had small excluded regions caused by the viscosity constraint.

Two evaluations were performed after the matrix design was complete, to avoid producing glasses with a segregated phase (salt or borate): 1) the predicted ILAW glass solubility limit for SO_3 with predicted uncertainty using the SO_3 solubility model ^[50] and, 2) use of the Taylor Rule to avoid creation of a borate rich phase ^[52]. Predictions of SO_3 solubility were performed after the final matrix was designed because it is not possible to predict the solubility of a component while simultaneously changing said component during the matrix design process. **Error! Reference source not found.** shows the target SO_3 and the predicted SO_3 solubility limit minus the prediction uncertainty (5.7×10^{-4} mass fraction) for each glass composition. SO_3 was batched at the target mass fraction when the predicted solubility was higher than the target. Otherwise, the SO_3 was batched at the predicted solubility limit minus the uncertainty to avoid making glasses with a segregated salt phase. The maximum SO_3 adjustment from the target to the predicted solubility limit was -0.0015 mass fraction. SO_3 was adjusted down to the predicted solubility limit and “Others” was renormalized back to its target composition using Eq. (1),

$$X'_i = X_i \times \frac{(\text{Others} - \text{SO}_3')}{(\text{Others} - \text{SO}_3)} \quad (1)$$

where:

X_i = mass fraction of the i th component of “Others”

X'_i = the renormalized mass fraction of the i th component of “Others”

Others = the target total mass fraction of the “Others” component

SO_3 = the target mass fraction of SO_3

SO_3' = the predicted SO_3 solubility limit

“Others” was renormalized to accommodate the small changes in SO_3 concentration to avoid altering the seven individually varied components. The resulting change to the “Others” composition is assumed to be insignificant because the largest SO_3 adjustment was 0.0015 mass %. The full target glass composition, for each glass, after SO_3 adjustment is provided in Table 4. Measured density from pycnometry, phase assemblage from XRD, and phase dimensions from SAXS are provided in Supplemental **Error! Reference source not found.**

Next, the Taylor rule was used to identify or estimate if any glass compositions will have the propensity for liquid-liquid phase separation into borate and silicate rich phases upon cooling from a melt. Peeler and Hrma found that the following equation, $Na_2O/(Na_2O+B_2O_3+SiO_2) \leq 0.2000$, conveniently distinguishes most of the glasses that have a propensity to phase separate from the compositions that do not ^[52]. Glasses with a value greater than 0.2000 generally will not phase separate a boron-rich phase from the silicate melt upon cooling. In supplemental **Error! Reference source not found.**, all glass compositions but eLAW03 are above the boundary (0.2000). eLAW03 is slightly below the 0.2000 boundary, at 0.1994 but because these glasses have more than the three components used in the Taylor Rule and they contain Al_2O_3 , which can suppress phase separation, this glass was not reformulated.

2.0 Experimental

2.1 Glass Fabrication

The glass compositions listed in Table 4 were batched using reagent grade chemicals in the form of oxides, carbonates, H_3BO_3 , Na_2SO_4 , NaF , NaPO_3 , and NaCl to ± 0.01 grams of the target masses. The batches were mixed in an agate milling chamber on the Angstrom shatterbox mill (Belleville, MI, USA), for 4 minutes, to homogenize the chemicals before melting. The batch was placed into a 90% platinum/10% rhodium crucible with a lid and melted at 1150 °C for 1 hour inside a Deltech DT31 furnace (Denver, CO, USA). Once melted, the glass melt was quenched (< 50 °C) on a stainless-steel plate. The quenched glass was milled to a fine powder in a tungsten carbide milling chamber on the Angstrom mill for 4 minutes to homogenize the glass. Powdered glass was then loaded back into the same 90% platinum / 10% rhodium crucible with a lid and remelted for a second 1-hour interval, quenched, powdered, and then repeated for a third, final 1-hour melt. The temperature of the second and third melts was raised above 1150 °C, max of 1350 °C, if visual observations from the preceding melts showed signs of SO_3 segregation or undissolved material upon quenching (see supplemental **Error! Reference source not found.**). This was done to improve the solubility of SO_3 salts or undissolved material into the glass phase. After the final melt the glass was poured into a bowl-shaped platinum crucible, covered by a lid, and slow cooled to room temperature following the canister centerline cooling (CCC) profile of a LAW canister ^[53]. Non-volatile major components (> 2 mass%) of all glasses in the matrix were confirmed to be on target (major element ± 15 mass %) by electron probe microanalysis (EPMA). Minor and trace components suffer higher uncertainty however they do not impact the overall glass composition. Semi-volatile components (B_2O_3 , Cl, F, SO_3 , and P_2O_5) showed retention factors between 80 % and 50 % of target, see measurements provided in the supplemental **Error! Reference source not found.**. Crystalline and amorphous phase homogeneities of the CCC heat treated glasses were investigated with X-ray diffraction (XRD) and small angle X-ray scattering (SAXS); small crystalline phases (ZnCr_2O_4 , $\text{Na}_2\text{CaSiO}_4$, and Na_2SO_4), in some glasses were observed, but no significant amorphous phase separation was observed (results provided in supplemental **Error! Reference source not found.**). The measured densities of the CCC heat treated glasses ranged from 2.60-2.76 g cm⁻³ by gas pycnometry and provided in **Error! Reference source not found.**.

2.2 Static Dissolution Testing with Zeolite Seeds

The experimental protocol and calculations of the seeded static dissolution experiments are given in detail in Parruzot et al. [27] and a summary is given here. The CCC glasses were prepared for static dissolution testing by milling the glass using a tungsten carbide milling chamber, followed by sieving to a size fraction of -100 to +200 mesh (150 to 75 μm). The sieved glass was washed and dried according to ASTM C1285-14 [54] and a portion of the cleaned glass was verified to be free of fines by scanning electron microscopy.

Crushed CCC glass was loaded into custom-made 80 cm^3 vessels made of 304 stainless steel with a sampling port used to pipette solution samples, measure pH, and add zeolite seeds. Static glass dissolution experiments were started by adding the target mass of glass powder (≈ 7.5 g), followed by gentle addition of ≈ 75 mL ultrapure ASTM D1193-06(2018) [55] Type 1 water to avoid resuspending the powder. All tests were started at a target glass surface area to solution volume ratio (S/V) of 2000 m^{-1} . Vessels were then sealed and heated in an electric thermostatically controlled oven to $90 \pm 2^\circ\text{C}$.

The solutions of the experiments were sampled regularly (see **Error! Reference source not found.**) which consisted of withdrawing solution aliquots (approximately 250 μL) from the reaction vessels using a micropipette. The aliquots were acidified to approximately 3 mL with $0.3 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ (BDH Aristar® Plus trace metal grade) for elemental analysis by ICP-OES. Masses of the solution aliquots and nitric acid additions were recorded for each sampling and used instead of solution volume to calculate elemental concentrations. The pH was also measured regularly at the test temperature through the top port, directly in the alteration vessel, with a glass pH electrode (Accumet™) calibrated at the same temperature with standard pH buffers.

The vessel mass was recorded before and after sampling to assess any loss caused by evaporation. ASTM Type 1 water was added to the vessel to compensate for solution lost by evaporation only, but not to offset the sampling volume. This was performed when the mass of solution in the vessel was found to deviate more than 0.5 g from the target solution mass at that time into the experiment.

The P2 type zeolite seeds were added to the reactor with the glass 28 days after starting the test. However, seeds were added 85 days after the start of the eLAW12 experiment. This decision was made because the glass dissolution rate had not slowed sufficiently to ensure that the anticipated acceleration effect of the seeds would be observed. Even with the delayed seeding for this glass, the total test duration was near one year.

To provide consistency throughout all experiments, the mass of zeolite seeds added was adjusted so that the outer surface area of the zeolite seeds in the experiment gave a zeolite S/V ratio equal to about half the glass S/V , geometrically estimated ^[56]. This equated to roughly 0.35 g of zeolite P2 seeds per reactor.

Acidified solution aliquots were quantitatively analyzed for major element concentrations by ICP-OES using a PerkinElmer Optima™ 8300 dual view instrument with an Elemental Scientific SC4 DX FAST auto-sampler. ICP-OES measurement error was within $\pm 10\%$, the maximum acceptable for calibration verification.

The normalized mass loss based on the release of element i in solution (NL_i , in g/m^2) values were calculated as described in Parruzot et al. ^[27]. The NL_i value allows comparison of relative durability of different glasses. Calculations performed here accounted for a decrease in the glass surface area (geometrically calculated) as reaction progress increased using a shrinking core model. However, it should be noted that the normalization using the surface area at the sampling time throughout the experiment is the most conservative hypothesis and leads to overestimate of NL_i at high fractions of glass altered. Rates discussed herein are mostly relative and refer to the relative increase of NL_i as a function of time for the 24 glass compositions studied.

The uncertainty for the NL_i values (displayed in the supplementary information) was calculated by error propagation and is based on the sources of experimental error during static dissolution test preparation and conduction. An uncertainty of $\pm 1\%$ was considered based on the error of the analytical balance for all measurements taken (glass initial mass, solution initial mass, solution samplings, mass of solution in vessel at each sampling). An uncertainty of $\pm 10\%$ was used for measured elemental concentration in solution by ICP-OES measurements.

3.0 Results

3.1 Behaviors before adding zeolite seeds

Zeolite seeds were added to each test reactor after 28 days of allowing the glass to react (Figure 2, data in supplemental **Error! Reference source not found.**). The general trend for the glasses was to corrode quickly before the dissolution rate slowed with time (i.e., transition from Stage I to Stage II behavior). The extent of reaction before seeding (times ≤ 28 days) varies widely between the different glasses. There appears to be no correlation between the extent of reaction before seeds to the extent of reaction after the addition of the zeolite to the system (see subsequent subsections). The glass with the highest NL(B) value at 28 days (eLAW05, 5.61 g m⁻²) corroded 40 times more than the lowest NL value (eLAW13, 0.14 g m⁻²). However, most glasses (20 of 24) have an NL(B) value at 24 days that passes the PCT-A metric for glass acceptance at WTP (2 g m⁻² at 7 days) ^[57]. These results show the range of relative extents of reaction progress after 24 days for the range of glass compositions used in this study.

3.2 Behaviors after adding zeolite seeds

Upon addition of the zeolite seeds to the reactor at 28 days, four types of behaviors based on boron release were observed and are also presented schematically in *Figure 3*:

1. Type 1: No observable effect after addition of seeds. There is no rate acceleration observed after zeolite addition and the alteration rate continues to decrease with time.
2. Type 2: The glass dissolution rate increases with the addition of seeds. The accelerated rate remains linear until the glass is completely altered.
3. Type 3: The glass dissolution rate increases with the addition of seeds but the increase in rate is transient.
4. Type 4: The glass demonstrates Stage III glass dissolution behavior, but the dissolution rate acceleration is offset with respect to the time the seeds were added.

The types of behaviors are discussed in the following subsections. Table 5 summarizes the dominant behavior demonstrated by each glass after the addition of the zeolite seeds. Behavior types were assigned based on the dominant behavior, although some glasses demonstrated traits from multiple behavior types. These behavior assignments only consider the first year of testing. The assignments of the different behavior types are subjective, and the observed behavior could change with longer testing. For this reason, the behavior assignments should be interpreted as qualitative descriptions of observed behavior. Table 5 also provides NL_B and pH values at select time periods throughout the experiment. The compositional factors that may be driving these behavior types are presented in a later section.

3.2.1 Type 1 – No change in behavior from zeolite addition

No rate increase was observed when zeolite seeds were added to reactors containing the following glasses: eLAW01, eLAW05, eLAW06, eLAW12, and eLAW16. The NL_B values for these glasses as a function of time are provided in Figure 4. The trend is nearly identical for the five glasses besides the extent of reaction, as indicated by the range in NL_B values that vary from 10.1 g m^{-2} for eLAW05 to 3.3 g m^{-2} for eLAW01 after 360 days of reaction. The pH ranged from 9.0 to 10.0 for the Type 1 glasses at the time when zeolite P2 seeds were added to the reactors. The average $\text{pH}_{90^\circ\text{C}}$ of the five Type 1 glasses was 9.3 ± 0.4 , which was the lowest average of the four behavior types after seeding. Interestingly, the rates, based on NL_B , of these glasses appear to be continually decreasing as the reaction approaches one year even though the Al concentration in solution slowly dropped after zeolite seeds were added (see Section 3.3). A drop in Al concentration is a common indication of zeolite growth. However, even if zeolites are growing, their growth is not causing a discernable increase in the extent of glass dissolution after one year of reaction. For these five glasses, it is possible that a relative fast release before zeolite seeding in the test masked any zeolite growth that is occurring in response to seeds.

3.2.2 Type 2 – Immediate Stage III glass dissolution behavior

For eight of the eLAW matrix glasses, a glass dissolution rate increase was concurrent with the addition of zeolite seeds. The increase in rate was sustained for the duration of the experiment or until completely dissolved. This set of glasses included eLAW02, eLAW04, eLAW08, eLAW10, eLAW11, eLAW13, eLAW14 and eLAW20. The NL_B values for these experiments are presented in Figure 5.

The eLAW02 glass rate was the fastest after the addition of the seeds and appears to have completely dissolved at 110 days after the addition of seeds. The other glasses that appear to completely dissolve after seed addition

and within the first year of testing are eLAW08 and eLAW14. Interestingly, before the addition of the seeds, eLAW02, eLAW08, and eLAW14 had an NL_B values of 1.7, 0.80, and 1.09 g m², respectively, which demonstrates that glass dissolution rates in various stages are not correlated. The pH of the Type 2 glasses ranged from 9.1 to 10.2 at the time zeolite P2 seeds were added to the reactors (28 d). The average pH_{90°C} of Type 2 glasses was 9.7±0.4, which was the highest of the four behavior types.

The remaining glasses that exhibited Type 2 behavior had various rates upon addition of seeds. eLAW04, eLAW10, eLAW11, and eLAW20 showed sustained and constant rates that were greater than pre-seeded rates. The increase of NL_B for these glasses as a function of time seems parallel. The last glass, eLAW13, showed an increase in rate with the zeolite seeds, but the acceleration in rate was small (see Figure 5b). Nevertheless, the increase in rate was noticeable and sustained for the duration of the experiment. This set of experiments highlights the widely divergent responses of glasses that have a sustained acceleration in rate upon zeolite seed addition.

3.2.3 Type 3 – Immediate Stage III glass dissolution behavior followed by rate decrease

For this set of glasses (eLAW03, eLAW07, eLAW18, eLAW19, and eLAW23), there was a noticeable increase in the glass dissolution rate after the zeolite seeds were added. However, the dissolution rate decreased, similar to the dissolution behavior of the glasses before seeds were added (Figure 6). The pH of Type 3 glasses ranged from 9.0 to 9.9 when the zeolite P2 seeds were added to the reactors. The average pH_{90°C} at seeding of Type 3 glasses was 9.5 ± 0.4, the second lowest average. The slowing in the rate after the acceleration observed after seeding occurs anywhere from 20 to 100 days after the seeds were added. This behavior is similar to behavior described in Strachan and Neeway^[33] where modeling by the authors showed the analcime growth rate was kinetically inhibited by the glass dissolution rate. The kinetics of zeolite growth and their effect on the glass dissolution rate at various pH values has been discussed previously^[2].

3.2.4 Type 4 - Progressive Stage III glass dissolution behavior

The fourth type of behavior that was observed was a progressive increase in the extent of glass dissolution with respect to time after seeding. After seeding, the six glasses took ≥ 120 days to fully accelerate to Stage III behavior (Figure 7). The progressive acceleration in rate indicates that the zeolite growth was or continues to be kinetically inhibited. Glasses that demonstrated this behavior were eLAW09, eLAW15, eLAW17, eLAW21, eLAW22, and eLAW24.

The rate and extent of alteration varied widely between the different glasses. For eLAW15 and eLAW22, where the full acceleration occurred at roughly 120 to 170 days after seeding, the accelerated rate continued until the glass was completely dissolved. For the remaining glasses, there was some indication that the rates were sustained (eLAW09, eLAW17) while other glasses show that the rate may once again be slowing with time (eLAW21 and eLAW24). The $\text{pH}_{90^\circ\text{C}}$ of Type 4 glasses ranged from 9.4 to 10.0 at the time when zeolite seeds were added to the reactor, and the average $\text{pH}_{90^\circ\text{C}}$ of the Type 4 glasses was 9.6 ± 0.2 .

4.0 Discussion

4.1 Link between pH and Stage III behaviors

High solution pH is one of the major factors that induce and sustain Stage III glass dissolution behavior according to the work by Neeway et al. [2], which systematically varied solution pH and observed that at $\text{pH}_{90^\circ\text{C}} \geq 11$, the AFCI glass studied showed a sustainable Stage III response (Type 2) to zeolite seeding while at $\text{pH}_{90^\circ\text{C}} < 11$ tests on the same glass showed only a brief Stage III response (Type 3). The effect of controlled pH on Stage III behavior was also demonstrated by Fournier et al. [28] on the international simple glass (ISG), where they performed zeolite seeded static dissolution tests at 90 °C and varied $\text{pH}_{90^\circ\text{C}}$ from 11.3 down to 10.1. The ISG glass responded with a linear acceleration at $\text{pH}_{90^\circ\text{C}}$ of 11.3 and 11.0, progressive acceleration at $\text{pH}_{90^\circ\text{C}}$ 10.7 and 10.4, and no acceleration was observed at $\text{pH}_{90^\circ\text{C}}$ 10.1 [28].

While pH wasn't systematically varied in this study, the $\text{pH}_{90^\circ\text{C}}$ of the solutions of these glasses varies from 9.0 up to 10.2 at the time of zeolite seeding based on the variable glass chemistry. After 360 days, the $\text{pH}_{90^\circ\text{C}}$ increased to 9.1 – 11. The strongest correlation between pH at 28 days and glass composition was achieved when plotting pH versus the total Na + K + Ca on a mole fraction basis ($R^2 = 0.91$, Figure 8a). The four behavior types are denoted with different symbols in Figure 8 along with the average pH of each behavior type. The $\text{pH}_{90^\circ\text{C}}$ of the individual glasses within each behavior type varies considerably, where the highest average pH belongs to the Type 2 and Type 4 glasses, followed by Type 3 and then Type 1. These trends hold as well when comparing Na + K + Ca to pH after 360 days of total experiment (~230 days after seeding, Figure 8b). Figure 8c shows the change in pH (i.e. ΔpH) from 28 to 360 days is largest for Types 4, then Type 2 (both sustained), followed by Type 3 (transitory), and the smallest was Type 1 (no response) Stage III response to seeds. These observations agree with previously published static dissolution testing results with zeolite seeds where pH was systematically varied on specific glasses [2,28].

For each of the behavior types, there are certain glass compositions that seem to be outliers in Figure 8. For example, eLAW01 exhibits a high pH (10.0 at 28 days) and high Na + K + Ca but does not seem to respond to seeds (Type 1). Interestingly, this glass has 1.3 mass % $\text{Na}_2\text{CaSiO}_4$ as a crystalline phase. Although we cannot say conclusively that the crystals affect the Stage III response, the two may be related.

4.2 Effect of Glass Composition on Seeded Stage III Response

Glass composition has an effect on the response to zeolite seeds observed in static dissolution tests as it controls overall stability of the glass structure, dictates the composition of alteration layers/secondary phases and dictates the ratio of dissolved components in solution, and hence the pH. A partition model was employed to identify boundaries within the composition space of the eLAW matrix for the four behavior types identified in Section 3. The partition model distinguishes data based on the relationship between the variables (glass composition) and the result (seeded response; i.e., Type 1, 2, 3 or 4) by evaluating all possible locations (composition boundaries) within the dataset. In this work, the JMP 12 partition model routine was used to identify the best possible partition(s) either as a positive (yes) or negative (no) response. To fit the partition models to categorical data (yes or no data) the JMP 12 software calculated an estimated nominal probability for each glass between 0 (no) and 1 (yes). We note that the assignments of the different behavior types are subjective, and this may influence the results of the partition model. Additionally, because the datasets are relatively small, removal or addition of one glass from one type to another will heavily influence the partition model outcomes. So though the assignments made by the partition model are provided as exact values, they should be interpreted as more qualitative and not quantitatively conclusive.

All of the major components varied in this study (Al_2O_3 , B_2O_3 , CaO , Na_2O , SiO_2 , SnO_2 , ZrO_2 , Others) and pH were evaluated simultaneously by the routine based on the three yes or no questions provided below:

- Question 1) Do the glasses show a Stage III response (Types 2, 3, & 4) rather than no response (Type 1)? (24 glasses evaluated.)
- Question 2) If yes to question 1, were Stage III responses sustained (Type 2 and 4) rather than transitory (Type 3)? (19 glasses evaluated.)
- Question 3) If yes to question 2, were sustained Stage III responses immediate (Type 2) rather than progressive (Type 4)? (13 glasses evaluated.)

Figure 9 shows the partition model for the glasses where zeolite seeds did or did not induce a Stage III response (Question 1). Glasses that showed a Stage III response are colored blue and glasses with no response are red.

All 16 Glasses with $\text{CaO} \geq 3.16$ mass % showed a Stage III response, either sustained (Type 2), transitory (Type 3), or progressive (Type 4). Glasses containing $\text{CaO} < 3.16$ mass% had a mixture of responses, where 3 glasses responded to seeding, and 5 glasses did not. This study clearly shows that CaO concentration in the glass influenced whether eLAW glass dissolution rates accelerated (i.e. induced Stage III behavior) in response to the zeolite P2 seed additions at 28 days. Three glasses (SRL202A, APCI and SON68) tested by Parruzot et

al. using the same seeded static dissolution testing method were plotted along with the eLAW glasses to show how the first partition model predicts glasses outside the eLAW matrix study^[27]. The $\text{CaO} \geq 3.16$ mass % for both AFCI and SON68 glasses and they were induced to Stage III behavior by seeding which agrees with the model boundary. However, SRL202A which has $\text{CaO} < 3.16$ mass %, was also induced to Stage III by seeding, similarly to three of the eLAW glasses.

Figure 10 shows the partition model for whether glasses showed a sustained Stage III response (Question 2). Sustainable (Type 2 and 4) versus transitory (Type 3) Stage III behavior was linked to the concentrations of Al_2O_3 and B_2O_3 . The first partition in the second partition model separates the composition space first at 7.93 mass % Al_2O_3 . Ten of eleven glasses with $\text{Al}_2\text{O}_3 \geq 7.93$ mass % had sustainable Stage III behavior after seeding. In the low $\text{Al}_2\text{O}_3 < 7.93$ mass % region a second partition at 11.36 mass % B_2O_3 was selected to further separate the sustained versus transitory responses to seeding. As a result, three of four eLAW glasses in the $\text{Al}_2\text{O}_3 < 7.93$ mass % and $\text{B}_2\text{O}_3 < 11.36$ mass % had sustained response to seeds. Whereas, three of four eLAW glasses with $\text{Al}_2\text{O}_3 < 7.93$ mass % and $\text{B}_2\text{O}_3 \geq 11.36$ mass % had a transitory response; similar to what was observed with SON68 (5.00 mass % Al_2O_3 , 14.14 mass% B_2O_3) by Parruzot et al.^[27]. Within the eLAW glass composition space the most susceptible glass compositions to sustainable Stage III behavior (Types 2 and 4) were high Al_2O_3 and low B_2O_3 . This is in agreement with Parruzot et al.^[27] where the AFCI glass (9.38 mass % Al_2O_3 , 9.65 mass% B_2O_3) also showed a Type 2 response.

Figure 11 shows partition model results for glasses that show an immediate (Type 2) versus those where the Stage III response was more progressive (Type 4). The results of this model showed that all eight of the Type 2 glasses had $\text{ZrO}_2 > 1.95$ mass %. Two of the Type 4 glasses contain $\text{ZrO}_2 > 1.95$ mass % while four contain $\text{ZrO}_2 < 1.95$ mass %. Zr content in the glass has been shown to be strongly correlated to glass corrosion behavior, where high Zr glasses have lower chemical durability compared to low Zr glasses^[58]. However, to our knowledge, the relationship between Zr and zeolite growth has not been explored. Thus, the relationship between Zr and the observed Type 2 and Type 4 behaviors deserves further investigation. The impactful effect of Ca can be explained both in terms of zeolite formation kinetics and the role of Ca in gel layer formation and stability. In terms of zeolite formation, Ca has recently been shown to increase the exothermicity of growth in initial oligomerization steps in silicate systems.^[59] These favorable thermodynamics may lead to faster zeolite formation kinetics. The faster formation kinetics of the zeolite are directly linked to increases in the glass dissolution rate either through an affinity effect associated with a decrease in orthosilicic acid activity^[32-34,60] or from destabilization of a passivating gel layer^[28,38]. Both processes are likely involved; however, decoupling the dissolution and growth of the two aluminosilicate phases remains difficult. In addition, Ca has also been

shown to be involved in calcium silicate hydrate (C-S-H) phase formation in alkaline conditions^[61-63].

Characterization of the solids once experiments are terminated would elucidate if a C-S-H phase formation may also be playing a role here.

According to the partition models, once the zeolite growth began then Al_2O_3 and B_2O_3 concentrations in the glass determined how sustainable the Stage III behavior was and in turn the zeolite growth process. Because Al_2O_3 was less abundant than the other zeolite components in the glass (Na_2O or SiO_2) its concentration in the glass can limit the growth rate of the zeolites. On the other hand B_2O_3 released from the glass becomes boric acid $[\text{B}(\text{OH})_3]$ in solution which buffers pH low. As discussed in the section above, pH is linked to both the Stage III rate and sustainability.

Another possible way to explain how CaO and Al_2O_3 in the glass contributed to Stage III behavior is to look at their roles in the gel layer that forms during the glass dissolution process. Ca compensates $[\text{AlO}_4]^-$ units during the gel and clay formation processes, leading to a stronger alumino-silicate networks with increased density. These stronger networks with increased densities decrease the water transport to contact the pristine glass, leading to a lower glass dissolution rate^[64]. When the zeolite seeds were added the Ca may counter diffuse from the surface layer alteration phases, including the gel, or directly from the glass dissolution process into the zeolite formation process. As the Ca^{2+} migrates out of the surface layer alteration phases it was likely replaced by something else, such as H^+ , in the surface layer alteration phases. This change reduced the protective behavior of the surface layer alteration phases, leading to accelerated glass dissolution to Stage III behavior, at which time CaO and Al_2O_3 limited the sustainability of the zeolite growth process as explained above.

5.0 Conclusions

Stage III behavior may have a large impact on elemental release of various nuclear waste glasses in a geological disposal environment. To further understand how various glass compositions influence Stage III rates in tests at 90 °C, a set of 24 glasses were tested to observe dissolution behavior when zeolite seeds were added to the system. The zeolite P2 seeded static dissolution method worked well at inducing Stage III glass dissolution behavior for 19 of 24 eLAW glasses at 90 °C. For the 19 glasses that demonstrated Stage III behavior, Types 2 and 3 showed an immediate acceleration in dissolution rate when seeded while Type 4 glasses demonstrated a progressive acceleration after seeding.

This was the first attempt, to our knowledge, to seed a matrix of glass compositions with the aim of understanding the impacts of individual elements on the alteration behavior after seeding. CaO, Al₂O₃, B₂O₃, and ZrO₂ concentrations in the glass were the most impactful on the response to zeolite P2 seeding at 90 °C in DIW for the eLAW matrix glasses. Their general effects on glass dissolution behavior after seeding is depicted in

Figure 12, and their specific effects were as follows:

- All 16 eLAW glasses with CaO $\geq$ 3.16 mass % showed a Stage III dissolution rate response to seeds, meaning Type 2, 3, or 4. Whereas five of eight eLAW glasses with CaO < 3.16 mass % did not respond to seeds (Type 1)
- Ten of eleven eLAW glasses with Al₂O₃ $\geq$ 7.93 mass % and three of four eLAW glasses with Al₂O₃ < 7.93 mass % and B₂O₃ < 11.36 mass % showed sustained Stage III glass dissolution behavior (Type 2 and 4). Whereas three of four eLAW glasses with Al₂O₃ < 7.93 mass % and B₂O₃ $\geq$ 11.36 mass% showed transitory Stage III behavior (Type 3).
- Type 2 behavior was differentiated from Type 4 by ZrO₂ concentration where, eight of ten eLAW glasses with ZrO₂ $\geq$ 1.95 mass % had Type 2 Stage III behavior and four of five eLAW glasses with ZrO₂ < 1.95 mass % showed progressive Stage III behavior (Type 4).

These compositional effects were also observed in glasses that were previously studied but are outside the eLAW design matrix. These highlight the effects of CaO and Al₂O₃, which are added as glass forming

chemicals but appear to lead to glasses that are more prone to Stage III behavior. When glasses have low CaO, Stage III behavior appears to be less likely. Glass dissolution experiments on this seeded eLAW glass matrix and unseeded tests are ongoing at at lower temperatures and 90 °C to determine the effect of temperature on the likelihood of Stage III behavior. Once the entire set of experiments are terminated, the induced Stage III rates will be calculated and those rates can be used by modelers to assess to impact of Stage III behavior in a selected repository system. Ultimately, a predictive composition parameter model will be developed to calculate the induced Stage III rate as a function of composition.

6.0 Acknowledgments

Funding for this work was provided by Washington River Protection *Solutions*, LLC and the authors would like to thank David Swanberg, Elvie Brown, Rodney Skeen and Ridha Mabrouki of Washington River Protection *Solutions* for programmatic guidance and support. The authors would like to thank Radha Motkuri for synthesizing the zeolite seeds used in this work. The SAXS portion of this research was conducted at the Advanced Photon Source (APS) beamline 9 ID-C. The authors thank Dr. Jan Ilavsky and the staff at beamline 9-ID,C for their assistance for data acquisition and analysis. Use of the APS, an Office of Science User Facility operated for the US DOE Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE- AC02-06CH11357.

7.0 References

- [1] S. Gin, A. Abdelouas, L. J. Criscenti, W. L. Ebert, K. Ferrand, T. Geisler, M. T. Harrison, Y. Inagaki, S. Mitsui, K. T. Mueller, J. C. Marra, C. G. Pantano, E. M. Pierce, J. V. Ryan, J. M. Schofield, C. I. Steefel, and J. D. Vienna, "An international initiative on long-term behavior of high-level nuclear waste glass," *Materials Today*, **16** [6], 243-248 (2013).
- [2] J. J. Neeway, B. P. Parruzot, J. F. Bonnett, J. T. Reiser, S. N. Kerisit, J. V. Ryan, and J. V. Crum, "Acceleration of glass alteration rates induced by zeolite seeds at controlled pH," *Applied Geochemistry*, **113**, 104515 (2020).
- [3] P. Van Iseghem, M. Aerstens, S. Gin, D. Deneele, B. Grambow, D. M. Strachan, B. P. McGrail, and G. G. Wicks, "GLAMOR - Or how we achieved a common understanding on the decrease of glass dissolution kinetics," pp. 115-126, *Proc. of the Ceramic Transactions*, **207**. Edited by A. Cosi and T. Ohji. Westerville, OH, 2009.
- [4] M. Collin, M. Fournier, P. Frugier, T. Charpentier, M. Moskura, L. Deng, M. Ren, J. Du, and S. Gin, "Structure of International Simple Glass and properties of passivating layer formed in circumneutral pH conditions," *npj Materials Degradation*, **2** [1], 4 (2018).
- [5] M. Fournier, T. Ducasse, A. Pérez, A. Barchouchi, D. Daval, and S. Gin, "Effect of pH on the stability of passivating gel layers formed on International Simple Glass," *Journal of Nuclear Materials*, **524**, 21-38 (2019).
- [6] T. Geisler, T. Nagel, M. R. Kilburn, A. Janssen, J. P. Icenhower, R. O. C. Fonseca, M. Grange, and A. A. Nemchin, "The mechanism of borosilicate glass corrosion revisited," *Geochimica et Cosmochimica Acta*, **158**, 112-129 (2015).
- [7] S. Gin, L. Neill, M. Fournier, P. Frugier, T. Ducasse, M. Tribet, A. Abdelouas, B. Parruzot, J. Neeway, and N. Wall, "The controversial role of inter-diffusion in glass alteration," *Chemical Geology*, **440**, 115-123 (2016).
- [8] C. Guittonneau, S. Gin, N. Godon, J. P. Mestre, O. Dugne, and P. Allegri, "A 25-year laboratory experiment on French SON68 nuclear glass leached in a granitic environment - First investigations," *Journal of Nuclear Materials*, **408** [1], 73-89 (2011).
- [9] S. Gin, X. Beaudoux, F. Angéli, C. Jégou, and N. Godon, "Effect of composition on the short-term and long-

term dissolution rates of ten borosilicate glasses of increasing complexity from 3 to 30 oxides," *Journal of Non-Crystalline Solids*, **358** [18–19], 2559-2570 (2012).

- [10] I. S. Muller and I. L. Pegg. 2018. *FY2018 Long-Term PCT of ILAW Glasses Final Report*. VSL-18R4510-1. Vitreous State Laboratory, The Catholic University of America, Washington, DC.
- [11] T. L. Goût, M. T. Harrison, and I. Farnan, "Impacts of lithium on Magnox waste glass dissolution," *Journal of Non-Crystalline Solids*, **517**, 96-105 (2019).
- [12] J. P. Icenhower and C. I. Steefel, "Dissolution rate of borosilicate glass SON68: A method of quantification based upon interferometry and implications for experimental and natural weathering rates of glass," *Geochimica et Cosmochimica Acta*, **157**, 147-163 (2015).
- [13] C. M. Jantzen, C. L. Trivelpiece, C. L. Crawford, J. M. Pareizs, and J. B. Pickett, "Accelerated Leach Testing of GLASS (ALTGLASS): I. Informatics approach to high level waste glass gel formation and aging," *International Journal of Applied Glass Science*, **8** [1], 69-83 (2017).
- [14] P. Jollivet, S. Gin, and S. Schumacher, "Forward dissolution rate of silicate glasses of nuclear interest in clay-equilibrated groundwater," *Chemical Geology*, **330–331**, 207-217 (2012).
- [15] J. J. Neeway, P. C. Rieke, B. P. Parruzot, J. V. Ryan, and R. Matthew Asmussen, "The Dissolution Behavior of Borosilicate Glasses in Far-From Equilibrium Conditions," *Geochimica et Cosmochimica Acta*, **226**, 132-148 (2018).
- [16] E. M. Pierce, L. R. Reed, W. J. Shaw, B. P. McGrail, J. P. Icenhower, C. F. Windisch, E. A. Cordova, and J. Broady, "Experimental determination of the effect of the ratio of B/Al on glass dissolution along the nepheline (NaAlSiO_4)-malinkoite (NaBSiO_4) join," *Geochimica et Cosmochimica Acta*, **74** [9], 2634-2654 (2010).
- [17] P. Frugier, S. Gin, Y. Minet, T. Chave, B. Bonin, N. Godon, J. E. Lartigue, P. Jollivet, A. Ayrat, L. De Windt, and G. Santarini, "SON68 nuclear glass dissolution kinetics: Current state of knowledge and basis of the new GRAAL model," *Journal of Nuclear Materials*, **380** [1-3], 8-21 (2008).
- [18] P. Frugier, T. Chave, S. Gin, and J. E. Lartigue, "Application of the GRAAL model to leaching experiments with SON68 nuclear glass in initially pure water," *Journal of Nuclear Materials*, **392** [3], 552-567 (2009).
- [19] B. Grambow and R. Müller, "First-Order Dissolution Rate Law and the Role of Surface Layers in Glass Performance Assessment," *Journal of Nuclear Materials*, **298** [1-2], 112-124 (2001).

- [20] B. P. McGrail, D. H. Bacon, J. P. Icenhower, F. M. Mann, R. J. Puigh, H. T. Schaefer, and S. V. Mattigod, "Near-field performance assessment for a low-activity waste glass disposal system: Laboratory testing to modeling results," *Journal of Nuclear Materials*, **298** [1-2], 95-111 (2001).
- [21] P. C. Rieke, S. Kerisit, J. V. Ryan, and J. J. Neeway, "Adaptation of the GRAAL model of Glass Reactivity to accommodate non-linear diffusivity," *Journal of Nuclear Materials*, **512**, 79-93 (2018).
- [22] T. Ma, A. P. Jivkov, W. Li, W. Liang, Y. Wang, H. Xu, and X. Han, "A mechanistic model for long-term nuclear waste glass dissolution integrating chemical affinity and interfacial diffusion barrier," *Journal of Nuclear Materials*, **486**, 70-85 (2017).
- [23] X. Feng and I. L. Pegg, "A glass dissolution model for the effects of S/V on leachate pH," *Journal of Non-Crystalline Solids*, **175** [2-3], 281-293 (1994).
- [24] P. Frugier, Y. Minet, N. Rajmohan, N. Godon, and S. Gin, "Modeling glass corrosion with GRAAL," *npj Materials Degradation*, **2** [1], 35 (2018).
- [25] W. L. Ebert and J. L. J. Jerden, "Parameterizing a Borosilicate Waste Glass Degradation Model " (2019).
- [26] J. V. Ryan, B. Parruzot, A. M. Lines, S. A. Bryan, L. M. Seymour, J. F. Bonnett, and R. K. Motkuri, "In-situ Monitoring of Seeded and Unseeded Stage III Corrosion using Raman Spectroscopy," *npj Materials Degradation*, **3** [1], 34 (2019).
- [27] B. P. Parruzot, J. V. Ryan, J. L. George, R. K. Motkuri, J. F. Bonnett, L. M. Seymour, and M. A. Derewinski, "Multi-glass investigation of Stage III glass dissolution behavior from 22 to 90 °C triggered by the addition of zeolite phases," *Journal of Nuclear Materials*, **523**, 490-501 (2019).
- [28] M. Fournier, S. Gin, P. Frugier, and S. Mercado-Depierre, "Contribution of zeolite-seeded experiments to the understanding of resumption of glass alteration," *npj Materials Degradation*, **1** [1], 17 (2017).
- [29] J. K. Bates and M. J. Steindler, "Alteration of Nuclear Waste Glass by Hydration." In *Scientific Basis for Nuclear Waste Management VI*, Vol. 15. Edited by D. G. Brookins. North-Holland, New York, NY, 1983.
- [30] W. L. Ebert, J. K. Bates, E. C. Buck, and C. R. Bradley, "Accelerated glass reaction under PCT conditions," *Materials Research Society Symposium Proceedings*, **294**, 569-576 (1993).
- [31] C. M. Jantzen, C. L. Trivelpiece, C. L. Crawford, J. M. Pareizs, and J. B. Pickett, "Accelerated Leach Testing of Glass (ALTGLASS): II. Mineralization of hydrogels by leachate strong bases," *International Journal of Applied Glass Science*, **8** [1], 84-96 (2017).

- [32] D. M. Strachan and T. L. Croak, "Compositional effects on long-term dissolution of borosilicate glass," *Journal of Non-Crystalline Solids*, **272** [1], 22-33 (2000).
- [33] D. M. Strachan and J. J. Neeway, "Effects of alteration product precipitation on glass dissolution," *Applied Geochemistry*, **45** [0], 144-157 (2014).
- [34] P. Van Iseghem and B. Grambow, "The long-term corrosion and modelling of two simulated Belgian reference high-level waste glasses," *Materials Research Society Symposium Proceedings*, **112**, 631-639 (1988).
- [35] M. Fournier, S. Gin, and P. Frugier, "Resumption of nuclear glass alteration: State of the art," *Journal of Nuclear Materials*, **448** [1-3], 348-363 (2014).
- [36] A. Papathanassiou, I. S. Muller, M. Brandys, K. Gilbo, A. Barkatt, I. Joseph, and I. L. Pegg. 2011. *ILAW Glass Testing for Disposal at IDF: Phase 1 Testing*. VSL-11R2270-1. Vitreous State Laboratory, Washington, DC.
- [37] S. Gin and J. P. Mestre, "SON 68 nuclear glass alteration kinetics between pH 7 and pH 11.5," *Journal of Nuclear Materials*, **295** [1], 83-96 (2001).
- [38] S. Mercado-Depierre, M. Fournier, S. Gin, and F. Angeli, "Influence of zeolite precipitation on borosilicate glass alteration under hyperalkaline conditions," *Journal of Nuclear Materials*, **491**, 67-82 (2017).
- [39] S. Gin, P. Jollivet, M. Fournier, C. Berthon, Z. Wang, A. Mitroshkov, Z. Zhu, and J. V. Ryan, "The fate of silicon during glass corrosion under alkaline conditions: A mechanistic and kinetic study with the International Simple Glass," *Geochimica et Cosmochimica Acta*, **151**, 68-85 (2015).
- [40] W. L. Ebert, A. J. Bakel, and N. E. Brown, "Measurement of the Glass Dissolution Rate in the Presence of Alteration Phases," pp. 569-575, *Proc. of the Spectrum '96*. Seattle, Washington, 1996.
- [41] A. Gauthier, J. H. Thomassin, and P. Le Coustumer, "Effect of some zeolitic materials on the R7T7 nuclear waste glass alteration," *Comptes Rendus DE L Academie Des Sciences Serie II Fascicule A-Sciences DE La Terre Et Des Planetes*, **329** [5], 331-336 (1999).
- [42] D. J. Wronkiewicz and K. A. Arbesman, "The role of alteration phases in influencing the kinetics of glass dissolution," *Materials Research Society Symposium Proceedings*, **608**, 739-744 (2000).
- [43] J. V. Crum, A. Y. Billings, J. B. Lang, J. C. Marra, C. P. Rodriguez, J. V. Ryan, and J. D. Vienna. 2009. *Baseline Glass Development for Combined Fission Products Waste Streams*. Pacific Northwest National Lab.(PNNL), Richland, WA (United States),

- [44] W. L. Ebert and J. K. Bates, "A Comparison of Glass Reaction at High and Low Glass Surface/Solution Volume," *Nuclear Technology*, **104** [3], 372-384 (1993).
- [45] B. Fleury, N. Godon, A. Ayral, and S. Gin, "SON68 glass dissolution driven by magnesium silicate precipitation," *Journal of Nuclear Materials*, **442** [1], 17-28 (2013).
- [46] R. L. Russell, B. P. McCarthy, S. K. Cooley, G. F. Piepel, E. A. Cordova, S. E. Sannoh, V. Gervasio, M. J. Schweiger, J. B. Lang, C. H. Skidmore, C. E. Lonergan, B. A. Stanfill, J. M. Meline, and J. D. Vienna. 2019. *Enhanced Hanford Low-Activity Waste Glass Property Data Development: Phase 2*. PNNL-28838. Pacific Northwest National Laboratory, Richland, WA.
- [47] P. Frugier, C. Martin, I. Ribet, T. Advocat, and S. Gin, "The effect of composition on the leaching of three nuclear waste glasses: R7T7, AVM and VRZ," *Journal of Nuclear Materials*, **346** [2], 194-207 (2005).
- [48] B. M. J. Thien, N. Godon, A. Ballesterro, S. Gin, and A. Ayral, "The dual effect of Mg on the long-term alteration rate of AVM nuclear waste glasses," *Journal of Nuclear Materials*, **427** [1], 297-310 (2012).
- [49] S. Narayanasamy, P. Jollivet, N. Godon, F. Angeli, S. Gin, M. Cabié, J. Cambedouzou, C. Le Guillou, and A. Abdelouas, "Influence of composition of nuclear waste glasses on vapor phase hydration," *Journal of Nuclear Materials*, **525**, 53-71 (2019).
- [50] J. Vienna, B. Stanfill, G. Piepel, B. Riley, D. Kim, S. Cooley, J. Crum, T. Jin, and C. Lonergan, "2016 update of Hanford glass property models and constraints for use in estimating the glass mass to be produced at Hanford by implementing current enhanced glass formulation efforts," *Pacific Northwest National Laboratory, Richland, WA*, (2016).
- [51] J. D. Vienna and J. V. Crum, "Non-linear effects of alumina concentration on Product Consistency Test response of waste glasses," *Journal of Nuclear Materials*, **511**, 396-405 (2018).
- [52] D. K. Peeler and P. R. Hrma. 1994. *PREDICTING LIQUID IMMISCIBILITY IN MULTICOMPONENT NUCLEAR WASTE GLASSES*. PNL-SA-23488. Pacific Northwest National Laboratory, Richland WA.
- [53] L. L. Petkus. 2003. *Low Activity Container Centerline Cooling Data*. Waste Treatment Plant, Richland, Washington.
- [54] ASTM C1285-14, "ASTM C1285-14 Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT)," ASTM International, West Conshohocken, PA, 2014.

- [55] ASTM D1193-06, "ASTM D1193-06 Standard Specification for Reagent Water," ASTM International, West Conshohocken, PA, 2018.
- [56] M. Fournier, "Étude Des Mécanismes À L'origine Des Reprises D'altération. Modélisation Et Évaluation De L'impact Sur Les Verres De Confinement," PhD Thesis, University of Montpellier, Montpellier, France, 2015.
- [57] J. Vienna, B. Stanfill, G. Piepel, B. Riley, D. Kim, S. Cooley, J. Crum, T. Jin, and C. Lonergan. 2016. *2016 update of Hanford glass property models and constraints for use in estimating the glass mass to be produced at Hanford by implementing current enhanced glass formulation efforts*. Pacific Northwest National Laboratory, Richland, WA.
- [58] C. Cailleteau, F. Angeli, F. Devreux, S. Gin, J. Jestin, P. Jollivet, and O. Spalla, "Insight into silicate-glass corrosion mechanisms," *Nature Materials*, **7** [12], 978-983 (2008).
- [59] E. E. Freeman, J. J. Neeway, R. K. Motkuri, J. D. Rimer, and G. Mpourmpakis, "Understanding Initial Zeolite Oligomerization Steps with First Principles Calculations," *AIChE Journal*, **in press** (2020).
- [60] W. L. Ebert and J. L. Jerden, "Parameterizing a Borosilicate Waste Glass Degradation Model " *npj Materials Degradation* **3**, 31 (2019).
- [61] C. A. Utton, R. J. Hand, P. A. Bingham, N. C. Hyatt, S. W. Swanton, and S. J. Williams, "Dissolution of vitrified wastes in a high-pH calcium-rich solution," *Journal of Nuclear Materials*, **435** [1], 112-122 (2013).
- [62] D. J. Backhouse, A. J. Fisher, J. J. Neeway, C. L. Corkhill, N. C. Hyatt, and R. J. Hand, "Corrosion of the International Simple Glass under acidic to hyperalkaline conditions," *npj Materials Degradation*, **2** [1], 29 (2018).
- [63] S. Liu, K. Ferrand, and K. Lemmens, "Transport- and surface reaction-controlled SON68 glass dissolution at 30°C and 70°C and pH=13.7," *Applied Geochemistry*, **61**, 302-311 (2015).
- [64] H. Aréna, D. Rébiscoul, E. Garcès, and N. Godon, "Comparative effect of alkaline elements and calcium on alteration of International Simple Glass," *npj Materials Degradation*, **3** [1], 10 (2019).

List of Tables:

Table 1. Individually varied components and their upper and lower bounds, in mass fraction

Component	Lower limit	Upper limit
Al ₂ O ₃	0.0600	0.1250
B ₂ O ₃	0.0600	0.1750
CaO	0.0000	0.1000
Na ₂ O	0.1500	0.2600
SiO ₂	0.3490	0.4700
SnO ₂	0.0000	0.0500
ZrO ₂	0.0100	0.0500
Others	0.0500	0.1640

Table 2. Composition of the “Others” component and their lower and upper limits, in mass fraction

Component	Others	Lower Limit	Upper Limit
Cl	0.0254	0.0013	0.0042
Cr ₂ O ₃	0.0549	0.0027	0.0090
F	0.0385	0.0019	0.0063
Fe ₂ O ₃	0.0732	0.0037	0.0120
K ₂ O	0.1220	0.0061	0.0200
MgO	0.0793	0.0040	0.0130
P ₂ O ₅	0.0824	0.0041	0.0135
SO ₃	0.0610	0.0030	0.0100
V ₂ O ₅	0.1220	0.0061	0.0200
ZnO	0.3415	0.0171	0.0560
Total	1.0000	0.0500	0.1640

Table 3. Multi-component constraints, in mass fraction

Constraint ID	Constraint
SO ₃ Solubility #1	$\text{Na}_2\text{O} + 0.66 \cdot \text{K}_2\text{O} \leq 0.2600$
SO ₃ Solubility #2	$\text{Na}_2\text{O} + 0.66 \cdot \text{K}_2\text{O} + 11.69 \cdot \text{SO}_3 \leq 0.3594$
Crystallinity	$\text{ZrO}_2 + \text{SnO}_2 + \text{Al}_2\text{O}_3 \leq 0.1700$
Viscosity at 1150 °C	$2 \leq \eta \leq 10, \text{ Pa} \cdot \text{s}$

Table 4. Target glass compositions in mass percent for the eLAW matrix (Note: eLAW omitted from Glass ID for brevity). characterization of the glass is provided in Supplemental **Error! Reference source not found.**

	Glass ID																							
	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Al ₂ O ₃	9.22	8.87	6.37	8.92	6.96	11.08	7.54	6.34	11.38	12.03	7.93	8.75	9.40	7.30	10.13	6.08	8.62	7.77	6.90	7.24	9.78	10.85	12.46	6.17
B ₂ O ₃	6.59	14.67	14.84	6.28	16.97	15.71	7.55	6.17	9.94	17.01	11.71	14.04	12.15	9.77	7.77	13.70	6.55	13.12	11.36	6.86	9.59	8.80	12.80	13.01
CaO	1.27	5.23	7.33	7.19	0.21	1.74	9.62	4.02	6.67	9.89	5.77	2.62	8.37	4.88	7.39	0.03	8.74	1.62	3.16	0.46	3.55	4.65	1.03	8.84
Na ₂ O	23.50	24.41	15.01	19.24	20.42	18.29	15.41	24.98	16.70	15.67	19.28	17.78	15.49	21.62	23.38	16.62	19.62	22.39	15.91	24.12	19.80	22.62	24.72	18.01
SiO ₂	39.78	37.51	45.46	35.68	42.91	38.81	42.36	42.63	38.00	35.02	43.48	41.51	40.95	35.02	39.37	46.00	46.81	36.44	39.00	44.65	40.63	44.50	35.28	36.16
ZrO ₂	1.59	2.32	4.89	4.52	1.79	4.63	3.12	4.20	1.63	2.62	2.51	1.08	1.95	4.27	3.83	2.07	1.36	3.26	4.82	4.96	3.29	1.52	1.40	1.52
SnO ₂	3.94	1.16	0.55	2.40	4.81	0.79	2.11	2.99	0.48	0.70	0.24	1.77	4.99	4.10	0.12	1.37	0.95	0.55	3.27	0.32	3.17	2.03	1.66	4.57
Cl	0.36	0.15	0.14	0.40	0.15	0.23	0.31	0.22	0.39	0.18	0.23	0.32	0.17	0.33	0.21	0.36	0.19	0.38	0.40	0.29	0.26	0.13	0.27	0.30
Cr ₂ O ₃	0.77	0.33	0.31	0.87	0.33	0.49	0.68	0.48	0.83	0.39	0.50	0.68	0.37	0.72	0.44	0.78	0.41	0.82	0.86	0.63	0.56	0.28	0.58	0.65
F	0.54	0.23	0.22	0.61	0.23	0.34	0.47	0.33	0.59	0.28	0.35	0.48	0.26	0.50	0.31	0.54	0.29	0.57	0.60	0.44	0.39	0.20	0.41	0.46
Fe ₂ O ₃	1.03	0.44	0.41	1.15	0.44	0.65	0.90	0.64	1.11	0.53	0.67	0.91	0.49	0.95	0.59	1.03	0.54	1.09	1.14	0.83	0.75	0.37	0.78	0.87
K ₂ O	1.72	0.73	0.69	1.92	0.73	1.09	1.50	1.06	1.85	0.88	1.12	1.52	0.82	1.59	0.99	1.72	0.91	1.81	1.90	1.39	1.24	0.62	1.30	1.45
MgO	1.12	0.47	0.45	1.25	0.47	0.71	0.98	0.69	1.21	0.57	0.73	0.99	0.54	1.03	0.64	1.12	0.59	1.18	1.24	0.90	0.81	0.40	0.84	0.94
P ₂ O ₅	1.16	0.49	0.47	1.30	0.49	0.74	1.01	0.72	1.25	0.59	0.76	1.03	0.56	1.08	0.67	1.17	0.61	1.23	1.28	0.94	0.84	0.42	0.88	0.98
SO ₃	0.86	0.23	0.25	0.96	0.32	0.55	0.73	0.51	0.93	0.31	0.47	0.76	0.37	0.80	0.41	0.86	0.37	0.88	0.95	0.69	0.62	0.27	0.65	0.56
V ₂ O ₅	1.72	0.73	0.69	1.92	0.73	1.09	1.50	1.06	1.85	0.88	1.12	1.52	0.82	1.59	0.99	1.72	0.91	1.81	1.90	1.39	1.24	0.62	1.30	1.45
ZnO	4.82	2.04	1.93	5.38	2.04	3.05	4.20	2.97	5.19	2.45	3.13	4.25	2.31	4.45	2.77	4.83	2.54	5.08	5.32	3.89	3.48	1.73	3.64	4.06
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 5. Summary of dissolution behavior types for the 24 eLAW glasses. See supplemental document 2

Glass ID	Behavior Type	7 days		28 days		49 days		145 days ¹		360 days ²	
		NL _B	pH ³	NL _B ⁴	pH	NL _B	pH	NL _B	pH ⁵	NL _B	pH
eLAW01	1	0.44	10.0	0.95	10.0	1.21	10.3	2.19	10.2	3.29	10.3
eLAW02	2	1.25	10.1	1.69	10.0	4.50	10.5	185.95	10.6	169.34	10.5
eLAW03	3	0.30	9.3	0.51	9.0	1.22	9.4	1.89	9.3	2.40	9.3
eLAW04	2	0.35	10.0	0.50	9.8	1.54	10.3	5.29	10.4	15.90	10.6
eLAW05	1	3.11	9.4	5.61	9.2	6.51	9.4	8.43	9.2	10.13	9.3
eLAW06	1	0.94	9.3	1.84	9.0	2.44	9.2	3.65	9.1	4.94	9.1
eLAW07	3	0.15	9.6	0.19	N/A	0.56	9.8	1.93	9.9	2.60	9.9
eLAW08	2	0.42	10.3	0.79	10.2	2.81	10.4	19.49	10.7	68.00	10.9
eLAW09	4	0.20	9.2	0.34	9.4	0.74	9.7	1.45	9.6	31.17	10.0
eLAW10	2	0.25	9.1	0.45	9.2	1.28	9.5	4.27	9.4	12.25	9.5
eLAW11	2	0.30	9.3	0.49	9.4	1.47	9.8	6.09	9.8	16.57	10.0
eLAW12	1	0.52	9.1	1.83	9.2	2.42	9.5	3.59	9.2	4.50	9.3
eLAW13	2	0.09	9.1	0.09	9.1	0.36	9.4	0.81	0.9	1.67	9.6
eLAW14	2	0.49	9.8	0.49	9.8	3.49	10.3	32.78	10.5	63.15	10.7
eLAW15	4	0.35	10.0	0.35	10.0	2.28	10.5	12.46	10.7	175.4	11.0
eLAW16	1	0.61	9.0	0.61	9.0	3.92	9.1	5.55	9.0	7.09	9.2
eLAW17	4	0.13	9.7	0.13	9.7	0.79	10.1	1.90	10.1	4.96	10.3
eLAW18	3	2.69	9.7	2.69	9.7	4.76	10.0	9.00	9.9	13.42	10.0
eLAW19	3	0.20	9.1	0.20	9.1	0.78	9.3	1.66	9.2	2.51	9.3
eLAW20	2	0.67	9.9	0.67	9.9	3.41	10.4	8.43	10.4	19.98	10.7 ⁶
eLAW21	4	0.23	9.4	0.23	9.4	0.63	9.8	1.22	9.8	2.84	9.1
eLAW22	4	0.20	9.7	0.20	9.7	1.04	10.2	4.66	10.3	205.1	10.8
eLAW23	3	2.30	9.9	2.30	9.9	3.94	10.2	7.53	10.2	10.30	10.4
eLAW24	4	0.31	9.5	0.31	9.5	2.45	9.9	6.83	9.9	26.89	10.3

¹ 139 days for eLAW01 to eLAW08; 147 days eLAW09 to eLAW16; 154 days for eLAW17 to eLAW24

² 386 days for eLAW01, and eLAW03 to eLAW08; 301 days for eLAW02; 373 days eLAW09 to eLAW16; 360 days for eLAW17 to eLAW24

³ The pH for eLAW01 to eLAW08 is measured at 13 days

⁴ Values for eLAW05, eLAW07, and eLAW08 at 23 days

⁵ eLAW11 to eLAW16 pH values from 167 days

⁶ pH from 338 days

List of Figures:

Figure 1. Scatter plot matrix of individually varied matrix components, in mass fraction. The minimum and maximum mass fraction for each component in the scatter plot matrix match those provided in Table 1. The figure highlights the wide compositional coverage range provided by the eLAW glass matrix.

Figure 2. (a) Normalized mass loss values as a function of time for 24 eLAW matrix glasses before P2 zeolite seeds were added to the reactor and (b) enlarged portion of shaded area of (a) for clarity. The eLAW glasses are categorized by their post-alteration behavior described in Section 3.2.

Figure 3. Schematic of the five dissolution behavior types observed in the Stage III dissolution tests. In all plots, the amount of glass altered is shown as a function of time and the vertical red line represents the zeolite addition time.

Figure 4. The normalized mass loss (NL_B) of the five glasses where no discernable change in glass dissolution behavior was observed upon the addition of zeolite seeds (Type 1 behavior). The vertical dashed line indicates the time when the zeolite seeds were added at 28 days.

Figure 5. (a) The normalized mass loss (NL_B values) of the eight glasses where an immediate and sustained increase in the glass dissolution rate was observed upon the addition of zeolite seeds (Type 2 behavior) and (b) enlarged portion of the shaded region of (a). The vertical dashed line indicates the time when the zeolite seeds were added.

Figure 6. The normalized mass loss (NL_B values) of the five glasses where an increase in the glass dissolution rate was observed upon the addition of zeolite seeds followed by a decrease in the rate (Type 3 behavior). The vertical dashed line indicates the time when the zeolite seeds were added. Individual plots more clearly show Type 3 behavior in the supplemental data.

Figure 7. (a) The normalized mass loss (NL_B) of the six glasses where an increase in the glass dissolution rate was observed at a time well after the addition of zeolite seeds (Type 4 behavior) and (b) enlarged portion of shaded region of (a). The vertical dashed line indicates the time when the zeolite seeds were added.

Figure 8. Na+K+Ca mol fraction in glass versus a) measured solution $pH_{90^\circ C}$ after 28 days of testing (when zeolite seeds were added to 90 °C static dissolution tests) and b) measured $pH_{90^\circ C}$ after 360 days. Experiments are grouped by behavior Type after seeding. Average pH and one standard deviation (indicated by error bars) are given for each Types. The c) average change in $pH_{90^\circ C}$ ($\Delta pH_{90^\circ C}$) from 28 days to 360 days with one

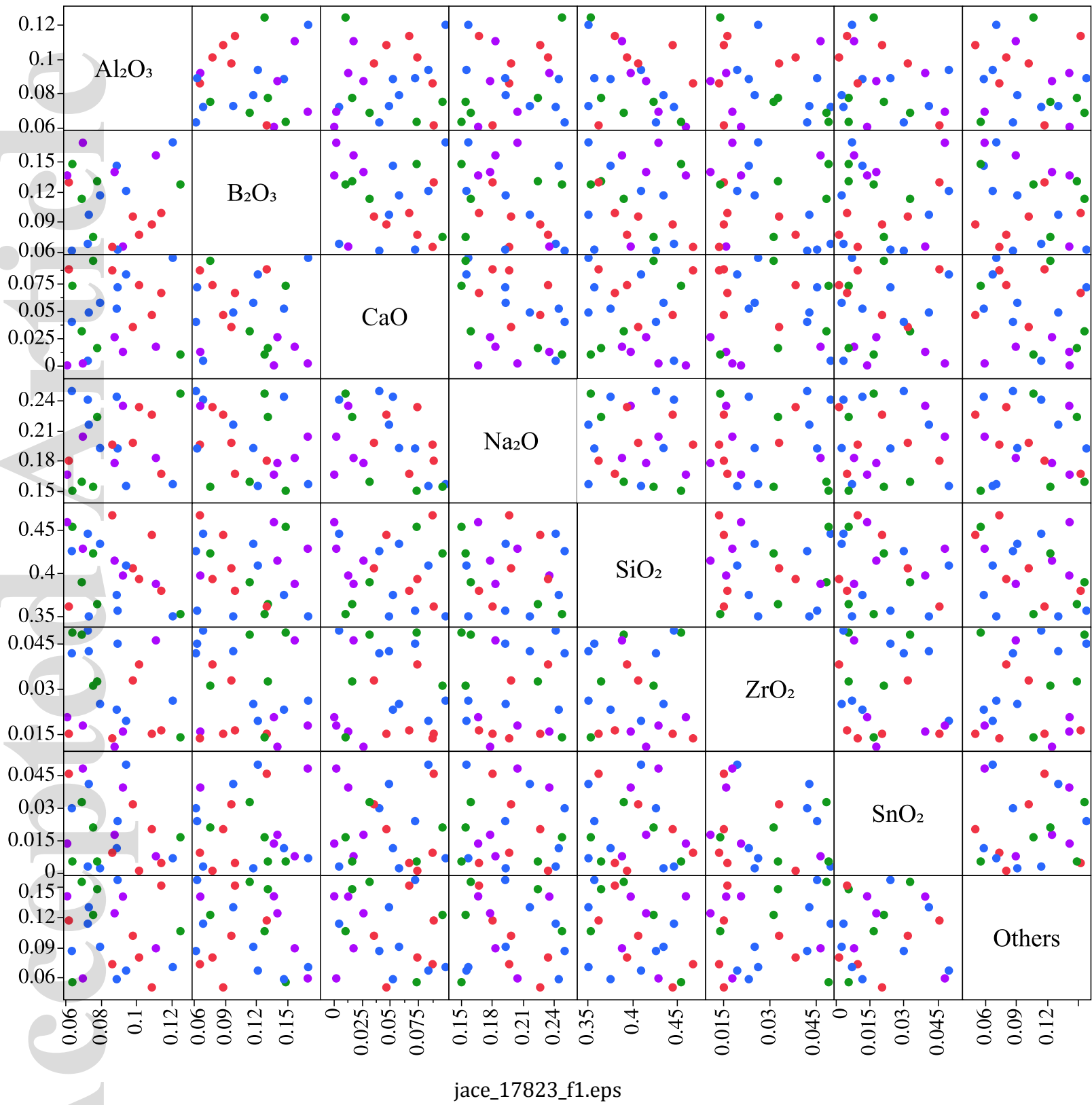
standard deviation for each Type are also shown. For eLAW21 (Type 4), $pH_{90^\circ C}$ at 318 days is reported as the eLAW21 $pH_{90^\circ C}$ at 360 days is an outlier in b) and c).

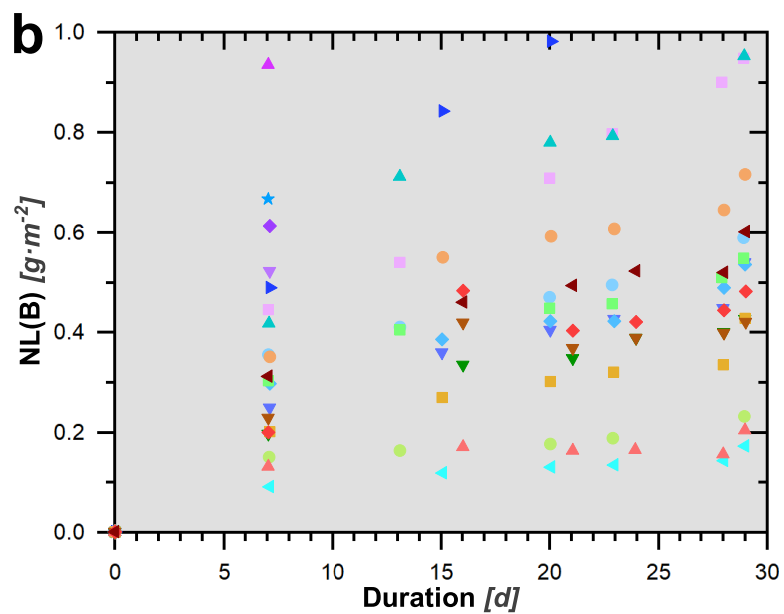
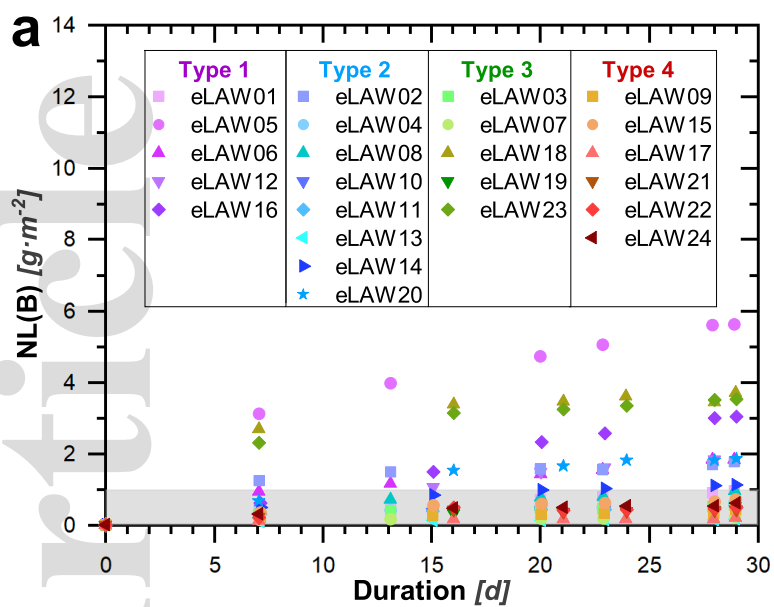
Figure 9. Partition tree for splitting glasses in the eLAW matrix where zeolite seeds induced a Stage III response (Type 1 vs. Types 2-3). x-axis is component concentration in glass and y-axis is estimated nominal probability between 1 (yes) and 0 (no). Only CaO was identified to discriminate between glasses that showed Stage III behavior and those that did not when zeolite seeds were added. The horizontal line separate yes (above) from no (below) in the compositional region identified on the x-axis. Symbol number denote behavior Type 1-4 and symbol color denotes glasses that responded to seeds (blue) versus glasses that didn't respond (red). Literature data from Parruzot et al. shown: X for glass SRL202A, Y for glass AFCl, and Z for glass SON68 [27].

Figure 10. Partition tree for splitting glasses in the eLAW matrix where zeolite seeds induced a linear Stage III response that was sustained (Type 2 or 4) or transient (Type 3). x-axis is component concentration in glass and y-axis is estimated nominal probability between 1 (yes) and 0 (no). Al_2O_3 was the most probable component for the first partition and B_2O_3 was the most probable for the second partition. The horizontal lines separate yes (above) from no (below) in the compositional region identified on the x-axis. Symbol number denote behavior Type 2-4 and symbol color denotes glasses that showed a sustained Stage III response (blue) versus glasses that showed a transitory behavior (red). Literature data from Parruzot et al. shown: X for SRL202A, Y for AFCl, and Z for SON68 [27].

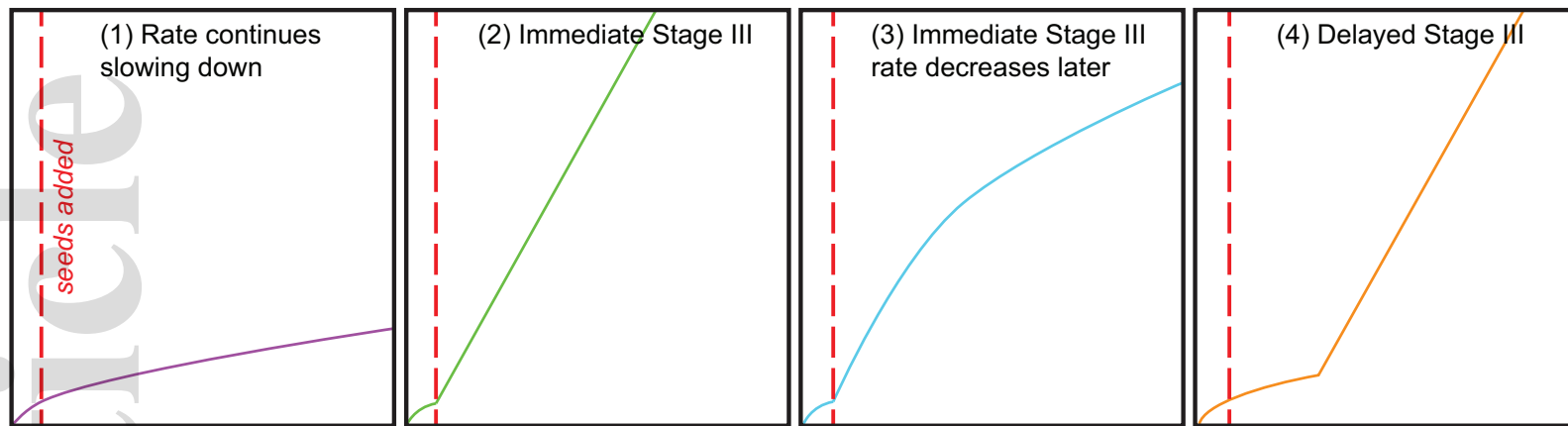
Figure 11. Partition tree for splitting glasses in the eLAW matrix where zeolite seeds induced a linear (Type 2) or progressive (Type 4) Stage III response. x-axis is component concentration in glass and y-axis is estimated nominal probability between 1 (yes) and 0 (no). The horizontal lines separate yes (above) from no (below) in the compositional region identified on the x-axis. Symbol number denote behavior Type 2 or 4. Literature data from Parruzot et al. shown: X for SRL202A, Y for AFCl, and Z for SON68 [27].

Figure 12. Schematic representation of the effect of CaO, Al_2O_3 , B_2O_3 , and ZrO_2 concentration in glass on the seeded glass dissolution behavior with time, where NL = normalized loss.



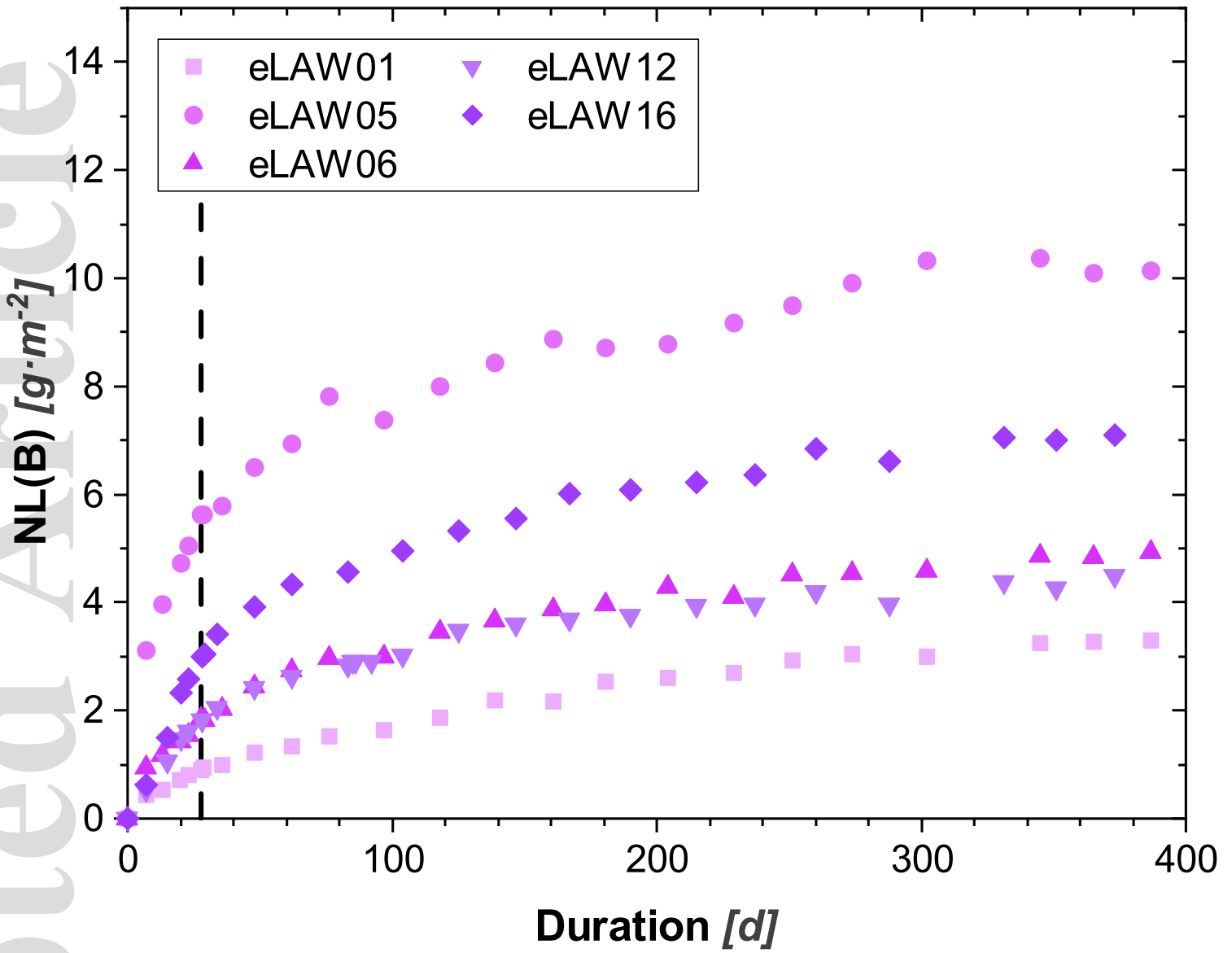


jace_17823_f2.eps

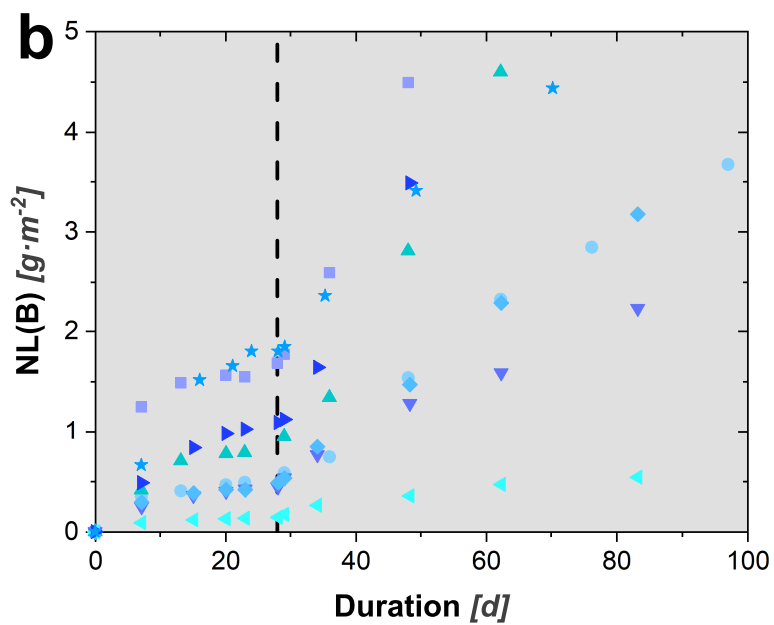
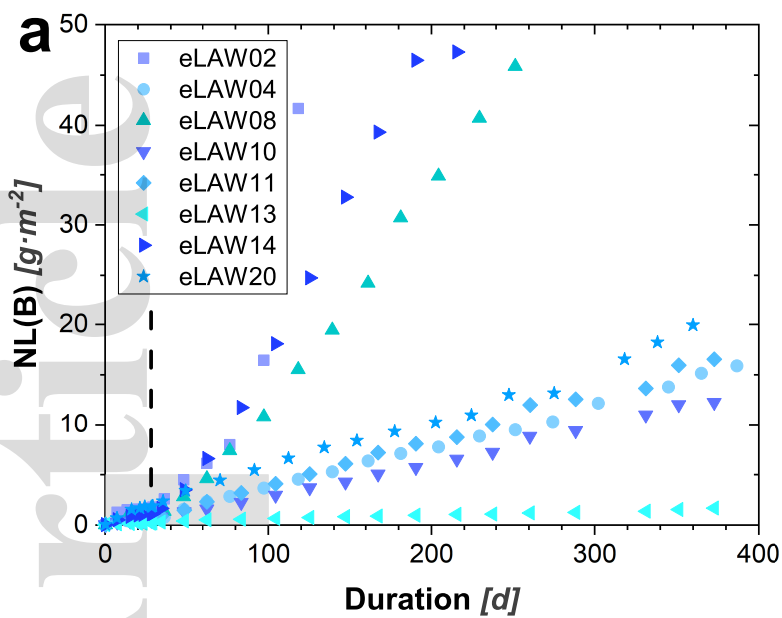


Duration

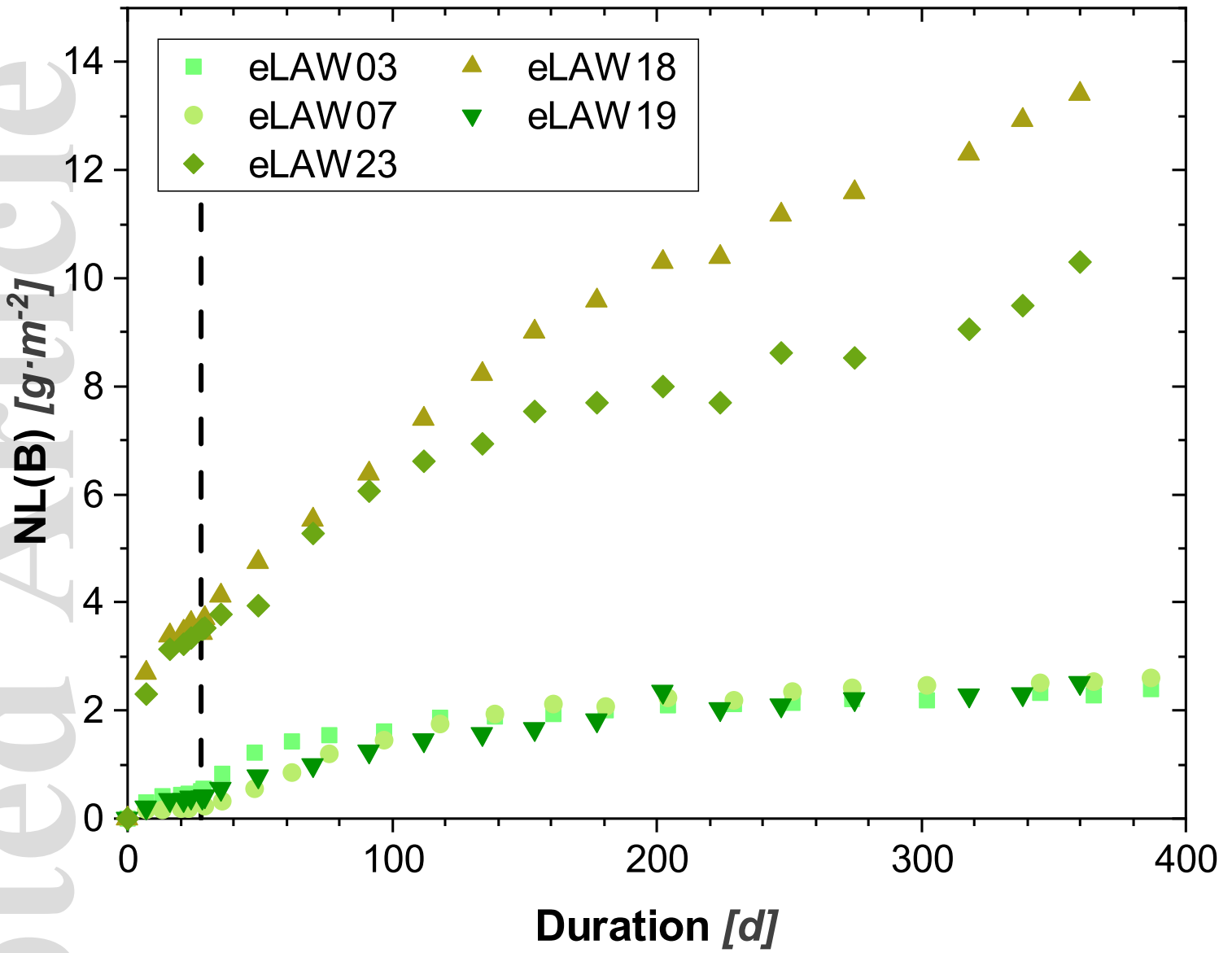
jace_17823_f3.eps



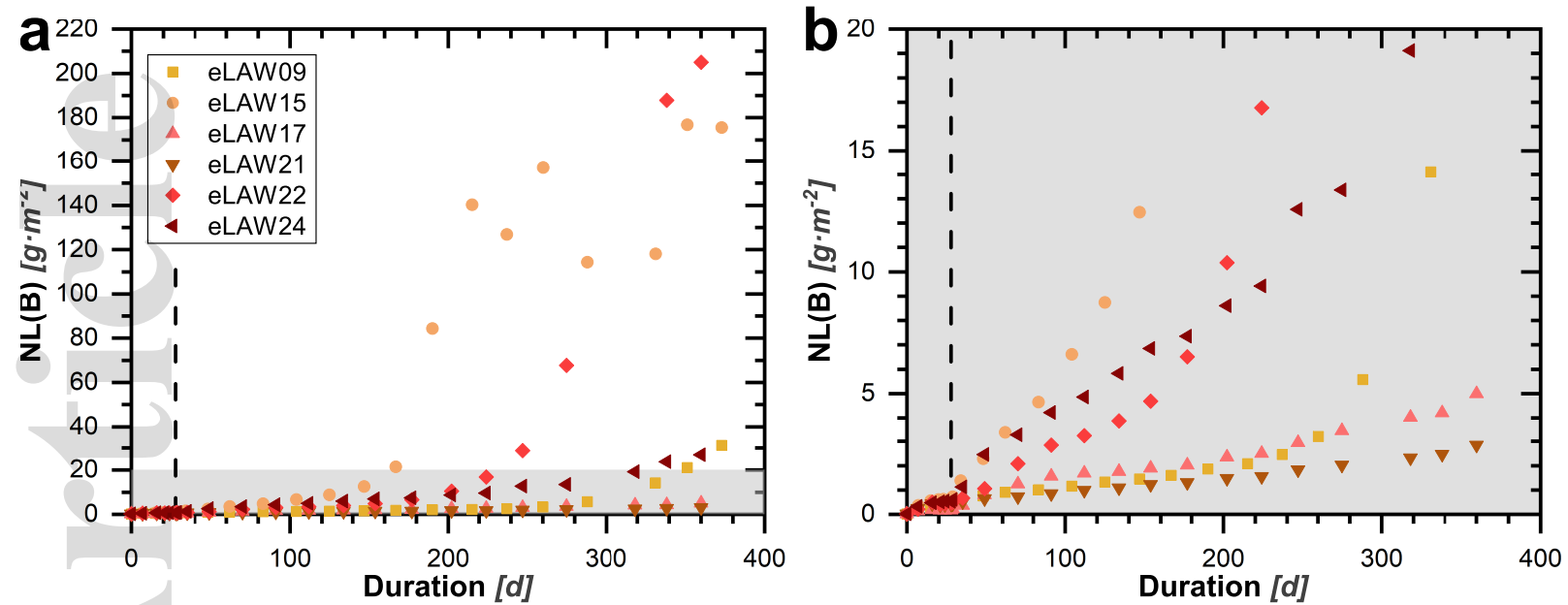
jace_17823_f4.eps



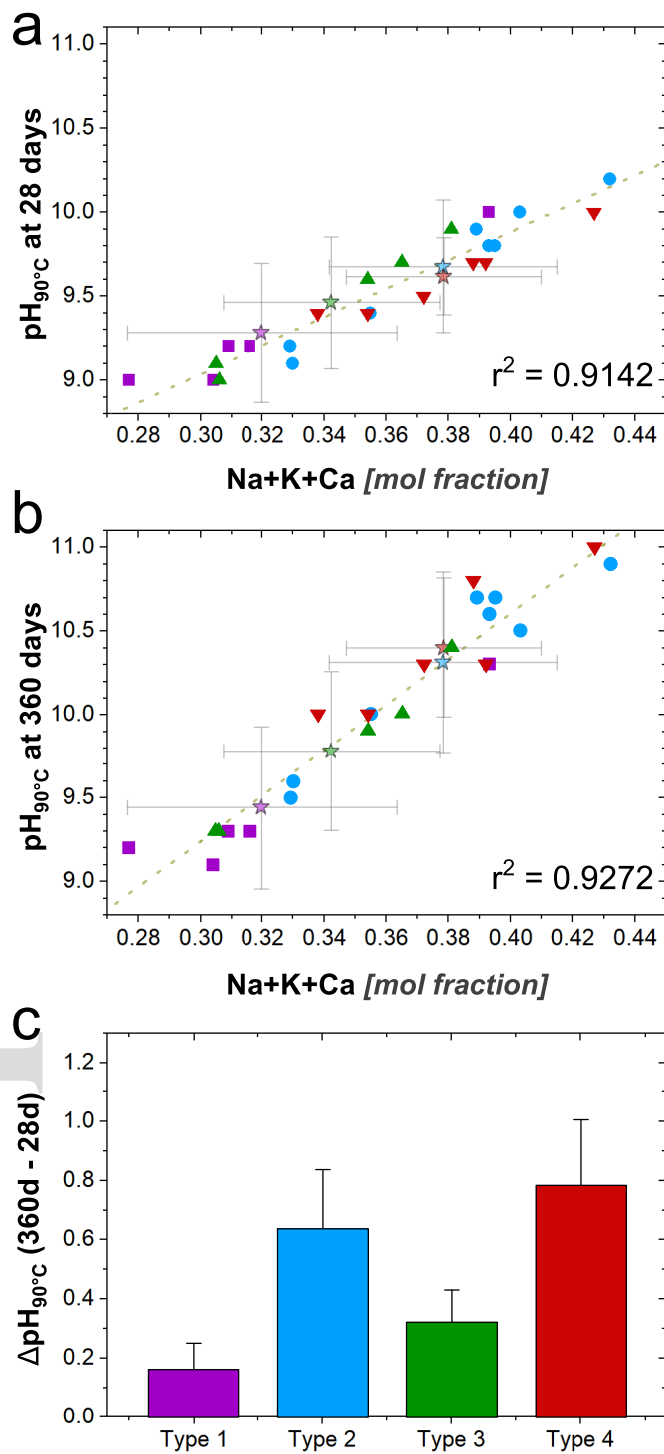
jace_17823_f5.eps

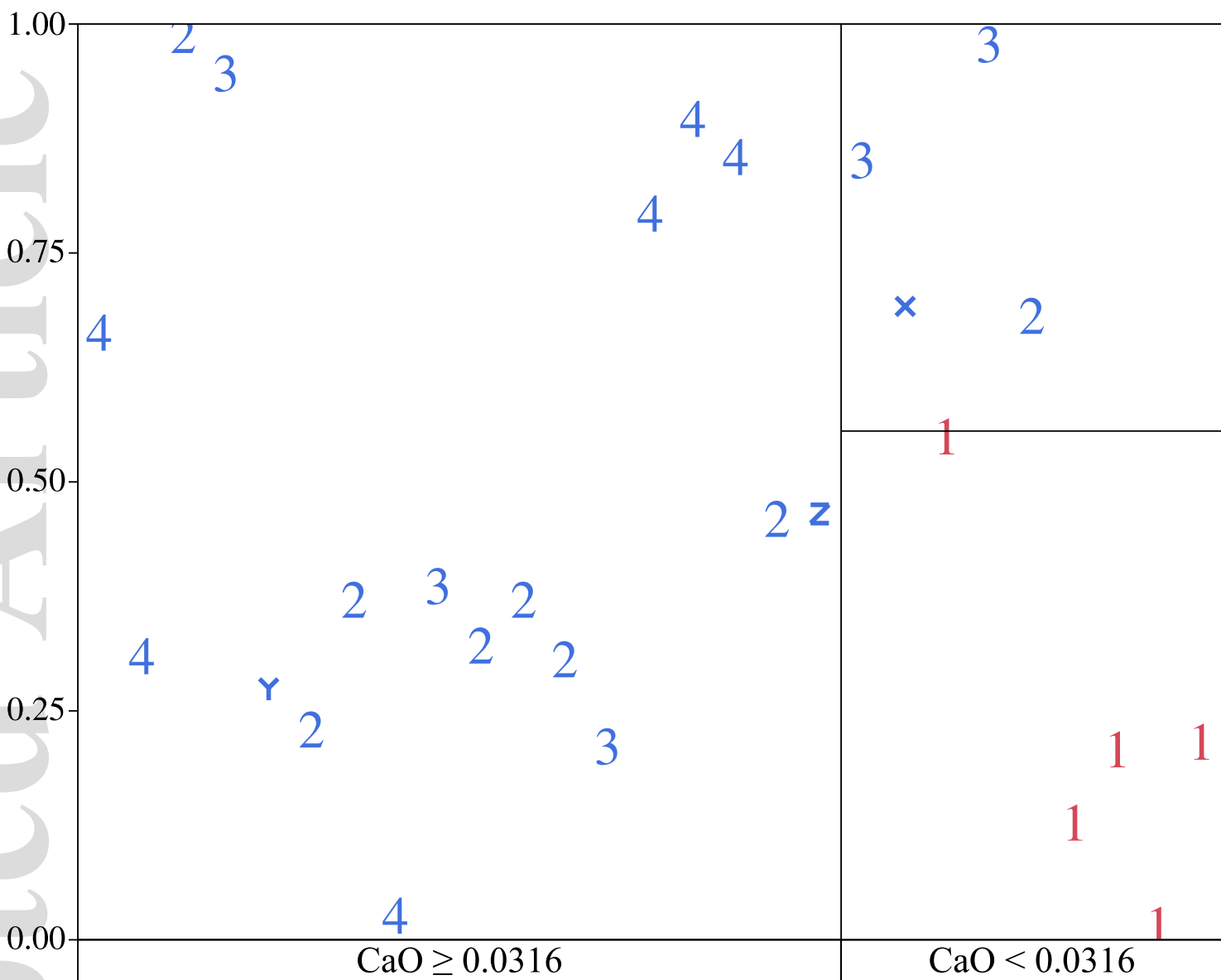


jace_17823_f6.eps



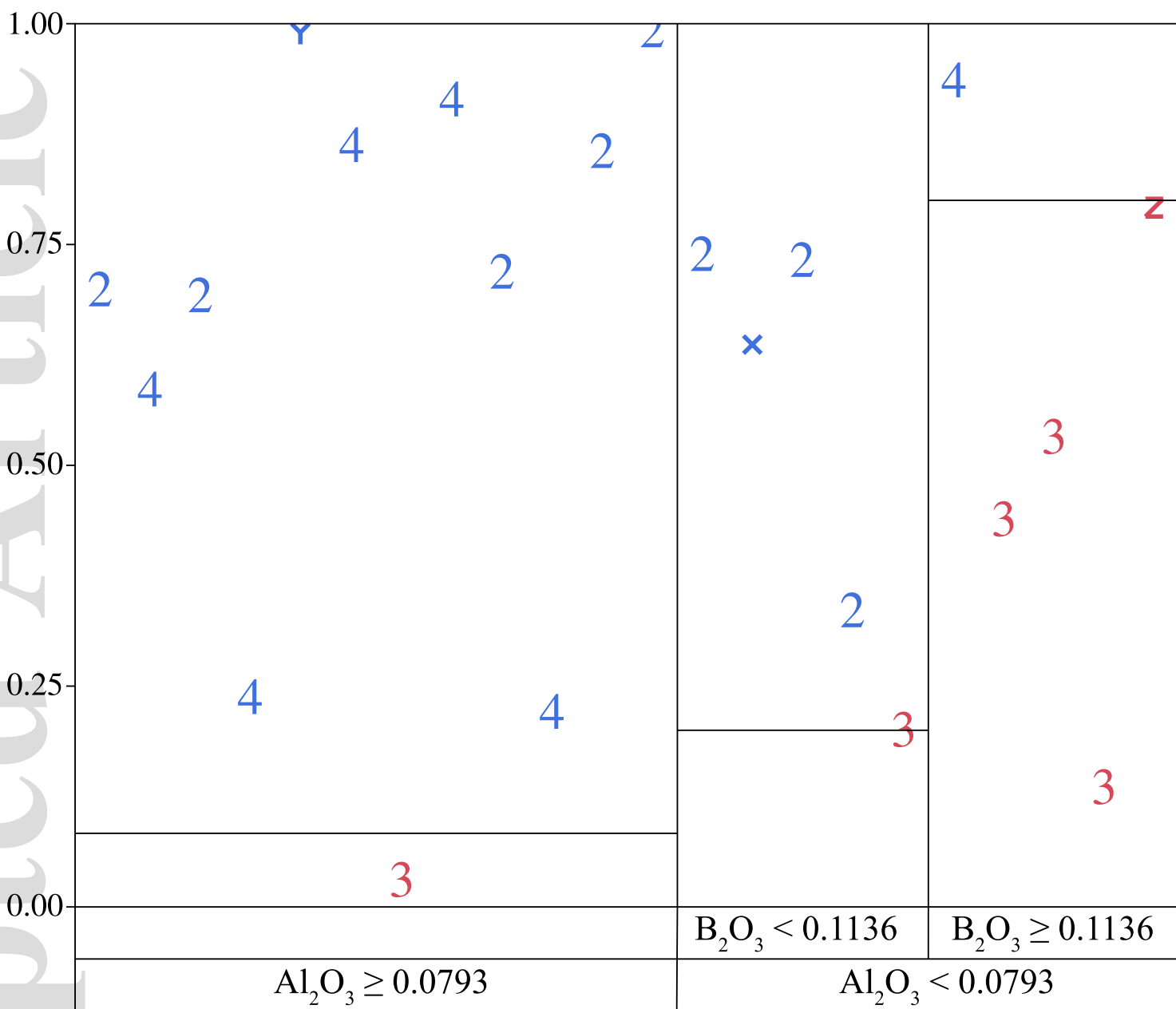
jace_17823_f7.eps



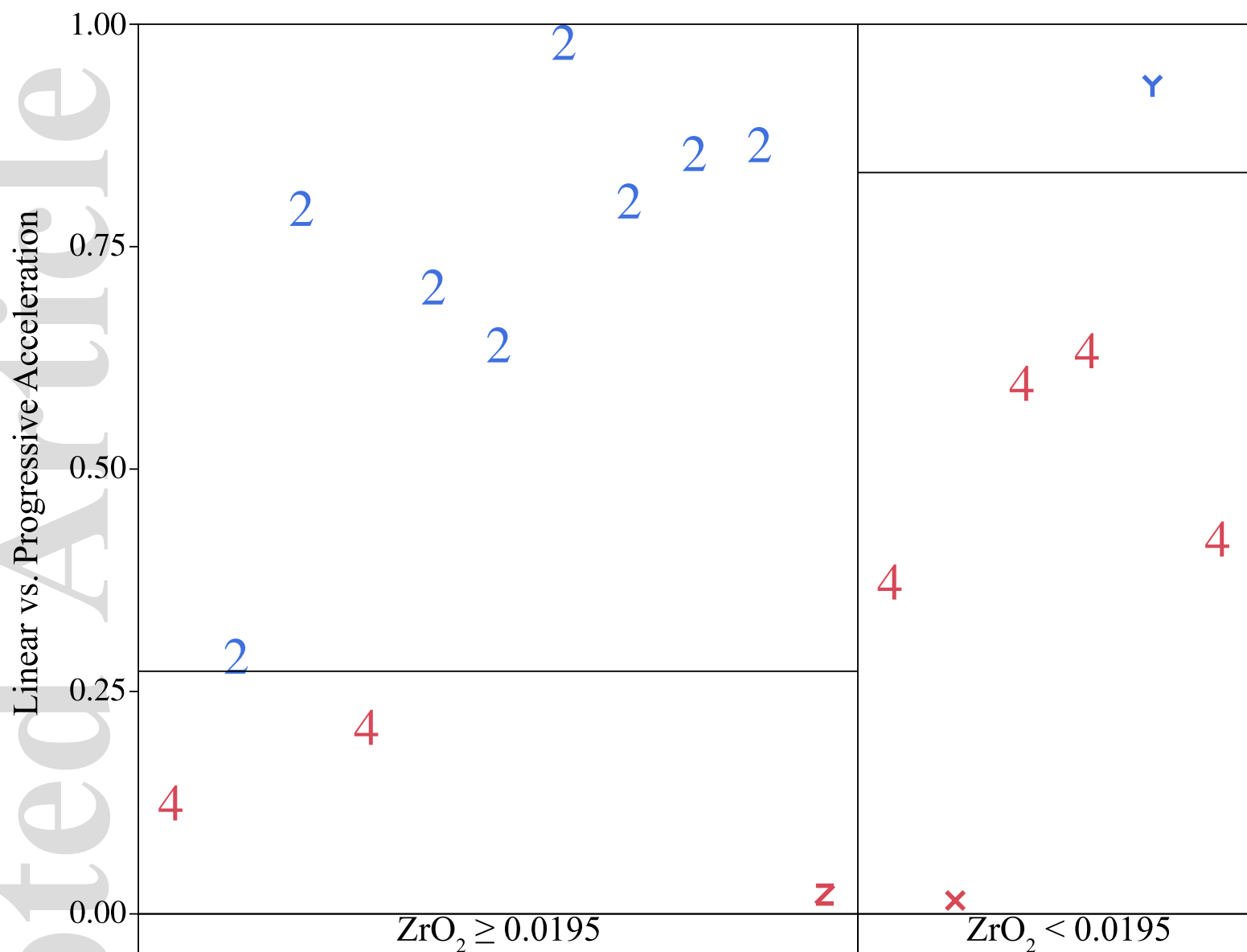


jace_17823_f9.eps

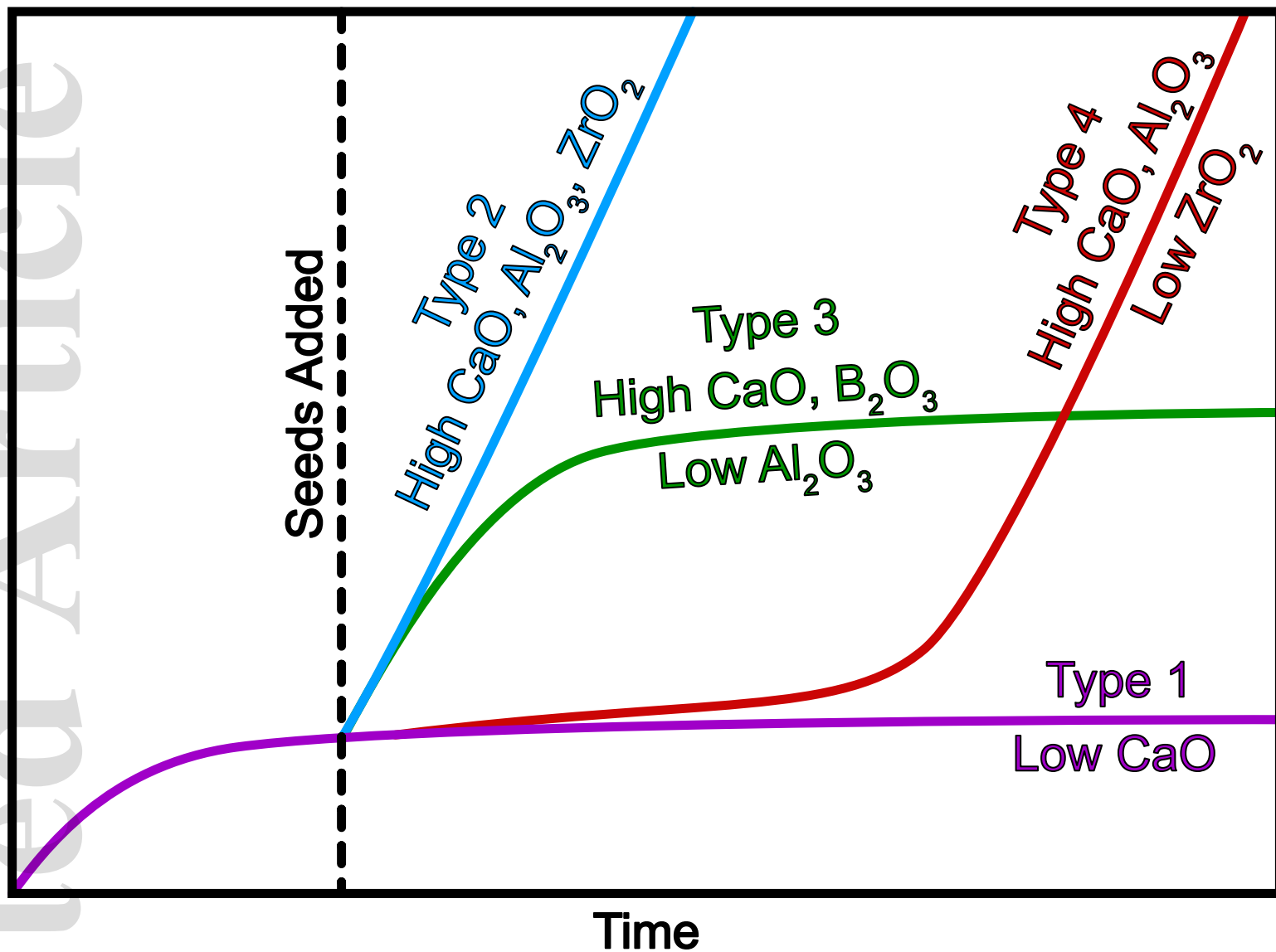
Sustained vs. Transitory Stage III Response



jace_17823_f10.eps



jace_17823_f11.eps



jace_17823_f12.eps