



# Sodalite as a vehicle to increase Re retention in waste glass simulant during vitrification



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## HIGHLIGHTS

- Re retention is improved by incorporation into sodalite structure.
- LAW-type glass shows lower retention but larger improvement with Re-sodalite.
- Sodalite is stable to higher temperatures in high-alumina glass melts.

## GRAPHICAL ABSTRACT

Glass	Re source	Re concentration (ppm)		Weight-loss factor	Retention	Relative % difference between Re-sodalite and Re <sub>2</sub> O <sub>7</sub>
		Pre-heat treatment	Post-heat treatment			
A0	Re-sodalite	73.0	83.7	0.775	0.889	20.5%
	Re <sub>2</sub> O <sub>7</sub>	70.4	66.8	0.777	0.738	
AN-102	Re-sodalite	65.8	37.3	0.838	0.475	84.9%
	Re <sub>2</sub> O <sub>7</sub>	81.7	25.1	0.836	0.257	

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## ABSTRACT

Technetium (Tc) retention during Hanford waste vitrification can be increased if the volatility can be controlled. Incorporating Tc into a thermally stable mineral phase, such as sodalite, is one way to achieve increased retention. Here, rhenium (Re)-bearing sodalite was tested as a vehicle to transport perhenate (ReO<sub>4</sub><sup>-</sup>), a nonradioactive surrogate for pertechnetate (TcO<sub>4</sub><sup>-</sup>), into high-level (HLW) and low-activity waste (LAW) glass simulants. After melting HLW and LAW simulant feeds, the retention of Re in the glass was measured and compared with the Re retention in glass prepared from a feed containing Re<sub>2</sub>O<sub>7</sub>. Phase analysis of sodalite in both these glasses across a profile of temperatures describes the durability of Re-sodalite during the feed-to-glass transition. The use of Re sodalite improved the Re retention by 21% for HLW glass and 85% for LAW glass, demonstrating the potential improvement in Tc-retention if TcO<sub>4</sub><sup>-</sup> were to be encapsulated in a Tc-sodalite prior to vitrification.

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## 1. Introduction

As a byproduct of the effort to produce plutonium for the US nuclear weapons arsenal from 1943 to 1988, a vast quantity of waste was produced at the Hanford Site in Washington State. This waste contains fission products and reagents from chemical separation processes and is largely stored in underground tanks [1]. Some of the tanks have leaked over the last few decades [2] and the waste must now be removed from the tanks and converted into a geologically stable waste form. The planned pathway for immobilizing the legacy waste is vitrification at the Hanford Tank Waste Treatment and Immobilization Plant (WTP) where the waste will be

mixed with glass-forming additives and converted into a glass waste form.

Technetium (Tc), specifically the <sup>99</sup>Tc isotope found in waste, is one of the more challenging components present in the legacy waste for a number of reasons. First, <sup>99</sup>Tc has a long half-life of  $2.13 \times 10^5$  y, so Tc will remain a primary dose contributor for the order of tens of thousands to hundreds of thousands of years [3]. Second, Tc is partly present in the waste as the pertechnetate ion (<sup>99</sup>TcO<sub>4</sub><sup>-</sup>), which is highly mobile in the environment. This represents a hazard to the waterways, communities, and ecology around the Hanford site [1]. Third, Tc is volatile at the temperatures where vitrification will be performed (circa 1150 °C) so keeping it in the melt during the vitrification process has proven difficult [4,5].

As a group VIIA element with stable isotopes, rhenium (Re) is a natural choice as a surrogate for radioactive Tc. Both Tc and Re have heptavalent states that are stable as either M<sub>2</sub>O<sub>7</sub> or more commonly

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$\text{MO}_4^-$  ( $M = \text{Re}^{7+}$  or  $\text{Tc}^{7+}$ ) [5]. The  $\text{TcO}_4^-$  (pertechnetate) and  $\text{ReO}_4^-$  (perrhenate) species dominate the environmental chemistries of these two elements, being stable, water soluble, and volatile [5,6]. While more reduced species of Tc and Re have dissimilar properties, especially in reduction potential for the lower oxidation states [3] and stability in glass melts [7], the  $\text{TcO}_4^-$  and  $\text{ReO}_4^-$  species have similar enough chemistries and volatilities that Re can be used as an effective surrogate for Tc. While a glass melt is sufficiently oxidizing, Tc/Re will remain in the heptavalent state and behave similarly [7]. The conditions in the early stages of the feed-to-melt reactions in air are oxidizing enough to make this assumption [8]. Indeed, the sodalite structure discussed in this paper includes  $\text{ReO}_4^-$  anions incorporated into the crystal lattice, and is thus expected to behave particularly similar to the Tc analogy [9].

Wastes to be vitrified at WTP are considered to be either low-activity waste (LAW) or high-level waste (HLW). While a large degree of variation can exist within these two categories, LAW glasses are high in Na and produced from tank salt cake and supernatant, while HLW glasses are high in Al and produced from tank sludge.

During the vitrification process, Tc/Re volatility increases as the temperature of the feed is increased as it contacts the melt surface. When Tc/Re volatilizes from the melter, it escapes into the off gas system, a system of filters and scrubbers that retain gaseous and vaporous components emanating from the melt surface. Only after this capture and repeated recycling into the melters can the majority of the Tc come to remain in the glass [10]. The off-gas scrubber also collects and recycles sulfur and halides back into the glass batch, which necessitates a lower waste loading, requiring a larger volume of glass and a longer, more expensive mission life. Thus, methods that could reduce, or even prevent, Tc volatility would be preferred over repeated recycling. The chemical mechanism of Tc volatility from, and incorporation into, glass is not fully understood and is affected by numerous variables including sulfate levels [11], foaming [4], and reducing agents added to the batch [5,6,11].

For LAW glasses, Re-retention has been measured to be between ~35 and 80% of initial values [10] and Re volatilizes during feed-to-glass transitions, with most of the volatility occurring between 600 and 900 °C [11]. The fate of Re (and subsequently Tc) in LAW is tied up with the behavior of the salt phase. Since the  $\text{TcO}_4^-$  anion is readily formed under the oxidizing conditions of the decomposing nitrates, the Tc/Re partitions into and migrates with the salt phase. As the nitrates, a principle component of the salt phase, continue to decompose, the Tc/Re either incorporates into the glass melt or volatilizes. Whether incorporated or volatilized, the fate of Tc/Re is largely decided by the time the salt phase has vanished at ~1000 °C, as in Fig. 1. Separating the Tc from the salt phase can increase its retention in the glass: when S is removed from the feed, the salt phase loses its principle component which can survive to high temperatures and the Tc/Re volatility decreases. Separating the Tc/Re from the salt phase by use of a mineral lattice should similarly decrease the volatility [12].

In HLW glass melts, Tc/Re volatility occurs at temperatures above 1000 °C, as in Fig. 1. HLW glasses tend to foam to low degree and thus Tc/Re volatility is driven by Henry's Law at high temperatures, rather than the species being driven off in effervescent feed-to-glass reactions. Overall, Tc/Re retention is often higher in HLW glasses than in LAW glasses, in part because of the lack of foaming and other volatility mechanisms at lower temperatures.

One approach to reduce Tc volatility during the vitrification process involves binding the Tc in a mineral lattice so that, rather than it being free in the feed slurry as  $\text{TcO}_4^-$ , it is present in a durable form with greater thermal stability, and thus lower volatility during the melting process. This type of approach is not currently in

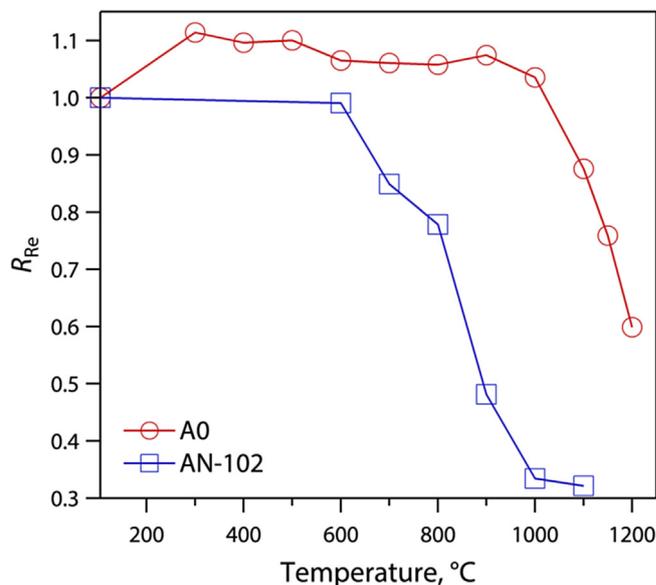


Fig. 1. The retention ratio of  $\text{Re}_2\text{O}_7$  ( $R_{\text{Re}}$ ) in A0 glass from Xu et al. [6] and in AN-102 glass from Jin et al. [12] during heat treatment.

practice at other vitrification facilities such as Savannah River's Defense Waste Processing Facility or Sellafield's Waste Vitrification Plant [13,14], where common practices include either tolerating volatility or separating volatiles during pretreatment, neither of which apply to current plans at WTP.

In order for a mineral phase to inhibit the volatility of Tc/Re, it must be intact at temperatures in the feed-to-glass transition when volatility would occur (Fig. 1). Because volatility of Tc/Re occurs at lower temperatures in LAW feeds than in HLW feeds, a mineral phase that survives to lower temperatures only may be effective in LAW feeds but not in HLW feeds. The differences in solubility and dissolution kinetics in the two glasses may confound this effect.

Finding suitable candidate minerals as hosts for Tc is not simple considering that no Tc-containing minerals are found in nature. Also, the chemistry and behavior of Tc is unique, and the best non-radioactive surrogate is  $\text{Re}^{7+}$ , which has similar chemistry to  $\text{Tc}^{7+}$ , whereas  $\text{Re}^{4+}$  is a poorer surrogate for  $\text{Tc}^{4+}$  [3,15]. However, over the past several years, several Tc-containing and Tc-surrogate (e.g., Re-containing) minerals have been synthesized in a laboratory setting and include perovskite (e.g.,  $\text{SrTcO}_3$ ) [16], pyrochlore (e.g.,  $\text{Ln}_2\text{Tc}_2\text{O}_7$ ) [16,17], spinel [15], and sodalite [9,18,19]. The composition of Re-sodalite has the general formula  $\text{Na}_8(\text{AlSiO}_4)_6(\text{ReO}_4)_2$  [18]. The current study is associated with the use of sodalite as a mineral host for  $\text{ReO}_4^-$ , an analogue for  $\text{TcO}_4^-$ -bearing sodalite.

A typical synthesis technique for making  $\text{ReO}_4^-$ -sodalite is a hydrothermal approach. When the aluminum and silicon ions encounter  $\text{ReO}_4^-$  at high pH, they form sodalite  $\beta$ -cages. Once coordinated inside these cages, the perrhenate ions cannot escape [19,20]. Fig. 2 shows the  $\text{ReO}_4^-$  tetrahedra at the center of the sodalite cage [18]. Sodalite is in the cubic space group  $P\bar{4}3n$  and includes 4- and 6-membered rings. The general formula  $\text{A}_8^I(\text{B}^{III}\text{C}^{IV}\text{O}_4)_6\text{D}_n$  sees  $\text{ReO}_4^-$  as the "D" in this species, with  $n = 2$ .

In the present study, Re-sodalite was added to the glass-forming feed batches of both HLW and LAW glass. The degree of Re-retention following the heat-treatments was measured by chemical analysis of the feed and the resulting glasses. This retention was compared to separate samples heat-treated under the same conditions but with  $\text{Re}_2\text{O}_7$  instead of Re-sodalite. To test the retention differences between these two Re sources, Re was added to feed at 100 ppm mass in respect to the mass of final glass.

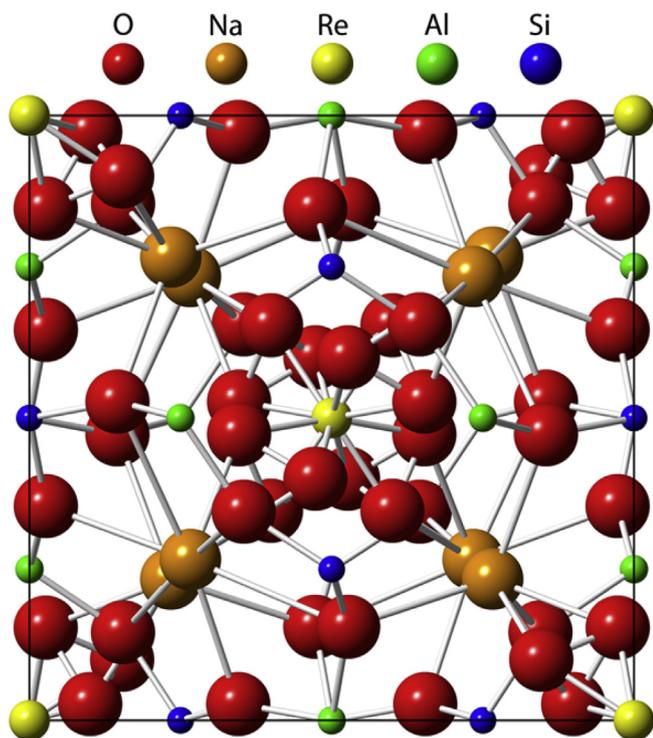


Fig. 2. Sodalite structure incorporating the perrhenate anion after Mattigod et al. [18].

To study the integrity of the sodalite structure in the glass melt, separate batches of both HLW (A0 [21]) and LAW (AN-102 [22]) feeds were prepared with 15 mass% Re-sodalite. These were divided into aliquots, heated to various temperatures, air quenched, and analyzed by X-ray diffraction (XRD). These samples are meant to examine the rate of decomposition of the Re-sodalite phase in each of the glasses being heat treated.

## 2. Experimental procedure

### 2.1. Re-sodalite preparation and characterization

The perrhenate sodalite,  $\text{Na}_8(\text{AlSiO}_4)_6(\text{ReO}_4)_2$ , used in the experiments was fabricated using a hydrothermal process described by Mattigod et al. [18]. Sodium perrhenate, sodium hydroxide, and sodium aluminate were dissolved in deionized water. This solution was combined with a solution of sodium silicate and reacted in a Teflon vessel at 175 °C for 24 h, forming a crystalline powder [19,20]. Crystallographic characterization was performed with a Bruker® D8 Advance (Bruker AXS Inc., Madison, WI) XRD with  $\text{Cu K}_\alpha$  emission and a LynxEye™ position-sensitive detector with a collection window of  $3^\circ 2\theta$ . Scan parameters were 5–70°  $2\theta$  with a step of  $0.015^\circ 2\theta$  and a 0.3-s dwell at each step. An internal standard of 5 mass% of  $\text{CaF}_2$  was used with each sample. Bruker AXS DIF-FRAC<sup>plus</sup> EVA was used for phase identification and Bruker AXS Topas v4.2 was used to conduct whole-pattern fitting with Rietveld refinement according to the fundamental parameters approach [23].

Particle size distribution (PSD) was carried out on a Malvern Mastersizer 2000 with a Hydro 2000G (Malvern Instruments Ltd., United Kingdom). Water was used as the dispersant. The solids concentration was 0.0121 vol%, with a refractive index of 1.483. Three levels of ultrasonic agitation were used to incrementally break apart agglomerations of the sodalite particles. Smaller particles were measured as ultrasonic treatment increased. For the

purposes of this paper, the most ultrasonicated analysis was assumed to be the most accurate characterized sample.

A JEOL JSM-7001F field emission gun scanning electron microscope (SEM; JEOL USA, Inc. Peabody, MA) was used to analyze the morphology of the sodalite in the experiments. Additionally, an EDAX Si-drift detector was used to conduct energy dispersive spectroscopy (EDS; Apollo XL, AMETEK, Berwyn, PA) for elemental spot analysis and dot mapping.

### 2.2. Preparing Re-retention samples

Four samples were prepared to test the retention of 100 ppm Re in glasses heat-treated to 1150 °C. Two glass batches were prepared using reagent-grade or higher purity starting materials. In order to represent typical HLW and LAW glasses, the A0 [21] and AN-102 [22] formulas, respectively, were selected. Table 1 shows the chemical constituents of the feeds for the glasses used. Re was added as either  $\text{Re}_2\text{O}_7$  or Re-sodalite to the glass feeds. Wet feed slurries of each glass were batched, and divided into aliquots. Four different types of samples were prepared where each glass (A0 or AN-102) was doped with 100 ppm Re, by mass, as  $\text{Re}_2\text{O}_7$  or  $\text{Na}_8(\text{AlSiO}_4)_6(\text{ReO}_4)_2$ . The feed slurries were stirred while drying on a hot plate, and finally heated in a 105 °C drying oven overnight until constant mass was achieved. The dried feeds were homogenized in a mill, and masses of feed equivalent to ~1 g of glass were loaded into Pt-10%Rh crucibles and placed into a Deltech furnace at room temperature. The furnace was then heated to 1150 °C at  $5^\circ\text{C min}^{-1}$ . Upon reaching temperature, the samples were removed from the furnace and air-quenched. These samples were characterized by inductively-coupled plasma mass spectroscopy (ICP-MS) and XRD.

To confirm the precision of this experimental set up, additional samples of  $\text{Re}_2\text{O}_7$  and Re-sodalite doped A0 were prepared as described above.  $\text{Re}_2\text{O}_7$  and Re-sodalite A0 feeds were independently re-batched using the same chemicals and dried. Two

Table 1  
Recipes of A0 [21] and AN-102 [22] feeds.

A0		AN-102	
Chemical	Mass (g)	Chemical	Mass (g)
$\text{Al}(\text{OH})_3$	367.49	$\text{Al}_2\text{SiO}_5$	86.23
$\text{H}_3\text{BO}_3$	269.83	$\text{H}_3\text{BO}_3$	175.27
$\text{CaO}$	60.79	$\text{CaSiO}_3$	135.82
$\text{Fe}(\text{OH})_3$	73.82	$\text{Fe}_2\text{O}_3$	51.93
$\text{Li}_2\text{CO}_3$	88.30	$\text{Li}_2\text{CO}_3$	78.49
$\text{Mg}(\text{OH})_2$	1.69	$\text{Mg}_2\text{SiO}_4$	31.04
$\text{SiO}_2$	305.05	$\text{SiO}_2$	316.52
$\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	2.67	$\text{TiO}_2$	13.29
$\text{Zr}(\text{OH})_4 \cdot 0.65\text{H}_2\text{O}$	5.49	$\text{ZnO}$	34.61
$\text{Na}_2\text{SO}_4$	3.55	$\text{Na}_2\text{SO}_4$	10.54
$\text{Bi}(\text{OH})_3$	12.80	$\text{ZrSiO}_4$	44.39
$\text{Na}_2\text{CrO}_4$	11.13	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	76.83
$\text{KNO}_3$	3.04	$\text{NaNO}_3$	82.66
$\text{NiCO}_3$	6.36	$\text{Na}_2\text{CO}_3$	42.98
$\text{Pb}(\text{NO}_3)_2$	6.08	$\text{NiO}$	0.08
$\text{Fe}(\text{H}_2\text{PO}_4)_3$	12.42	$\text{PbO}$	0.08
$\text{NaF}$	14.78	$\text{NaF}$	1.72
$\text{NaNO}_2$	3.37	$\text{NaNO}_2$	56.59
$\text{Na}_2\text{C}_2\text{O}_4$	1.26	$\text{Na}_2\text{C}_2\text{O}_4$	1.26
$\text{NaOH}$	99.41	$\text{NaOH}$	46.19
		$\text{KOH}$	6.44
		$\text{NaCl}$	3.25
		$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	1.28
		$\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$	2.41
		$\text{NaHCO}_2$	21.75
		$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	6.61
		$\text{C}_2\text{H}_4\text{O}_3$	26.72
		$\text{C}_6\text{H}_8\text{O}_7$	7.84

duplicate samples equivalent to 1 g of glass for each feed were added to Pt crucibles and heat treated to 1200 °C. All four samples were removed upon reaching temperature and air quenched. Then, they were prepared for ICP-MS characterization.

### 2.3. Preparing phase analysis sample

Two series of samples were prepared to characterize the durability of Re-sodalite during the feed-to-glass transition. Glass feeds of A0 and AN-102 were prepared as above as wet slurry, and doped with 15 mass% Re sodalite. These samples were likewise dried to a constant mass and homogenized in a mill. Masses equivalent to 1 g were added to Pt-10%Rh crucibles and placed into a Deltech furnace at room temperature. The furnace was ramped at 5 °C min<sup>-1</sup> to 400, 600, 800, 1000, 1100, or 1200 °C. Immediately upon reaching the target temperature the samples were removed and air quenched.

### 2.4. Post heat-treatment and characterization

Heat treated samples were broken out of the Pt crucibles. The heat treated sample and dried feeds were homogenized by hand in an alumina mortar and pestle and analyzed with XRD. The ICP-MS analysis was performed by Southwestern Research Institute (San Antonio, TX) on powdered Re-retention samples. Phase analysis samples were not analyzed by ICP.

## 3. Results and discussion

### 3.1. Characterization of as-made Re-sodalite

The sodalite prepared was found to be suitable for the experiments. The purity was satisfactory and the particle sizes were comparable to the sizes of other Tc-bearing waste forms being targeted to improve Tc incorporation into glass [24].

The PSD of the Re-sodalite showed a multimodal size distribution. The spectrum included four maxima and a bulk of the particles falling within the range of 1–100 μm but also with fines (<1 μm) and larger agglomerates (100–1000 μm). Concurrent and yet-to-be-published research on Tc-containing mineral phases to be added to glass melts have targeted >1 μm particle sizes, so the sodalite used here was comparable to that target.

According to the XRD pattern shown in Fig. 3a, the as-made Re-sodalite contained a small fraction of unreacted NaReO<sub>4</sub> (3.2 mass %), the majority phase was Re-sodalite (76.3 mass%), and contained a residual phase (20.5%) that appeared amorphous. This amorphous phase likely consisted of tiny sodalite crystals seen during PSD and SEM analyses (Fig. 3b and c). While such fine particles are not ideal with respect to the target sizes, they were not anticipated to interfere with the experiment. The particle size will influence the kinetics of the sodalite reacting with the melt, but will not change the identity of those reactions. As a comparative measure between the two feeds used (LAW and HLW), keeping the size distribution of the sodalite particles consistent was sufficient to draw conclusions upon the results obtained with this starting material.

Elemental spot analysis with EDS showed compositional homogeneity across the range of particle sizes present, in addition to a Re-rich phase that appeared brighter than the sodalite grains; this phase was suspected to be NaReO<sub>4</sub> following the XRD results of the as-made material. This indicated that the predominant phase, the Re-sodalite, is made up of particles of various sizes, and supports the conclusion that the fine particles seen during SEM analysis were in fact small sodalite particles. This also supports the hypothesis that the amorphous phase detected by XRD was likely the signal from the fine sodalite particles.

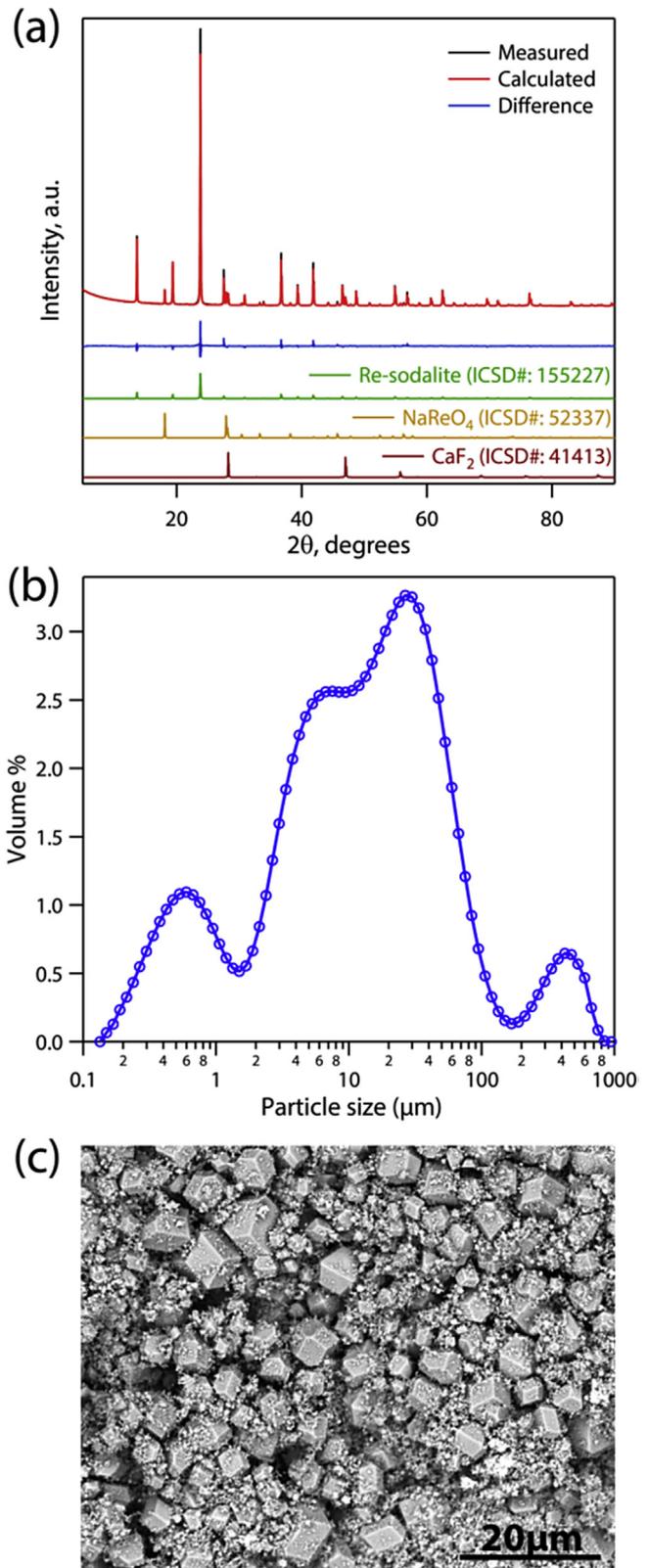


Fig. 3. Characterization of as-made rhenium sodalite including (a) XRD, (b) PSD (sonicated), and (c) SEM.

The unreacted NaReO<sub>4</sub> in the sodalite was not ideal but it was not critical to the experiment and should have been present in the same concentration as was used for all experiments. One of the purposes of using the Re-sodalite was to determine if the different

structural environments of Re in sodalite as opposed to free  $\text{ReO}_4^-$  affects the retention; a minor contamination of 3.2 mass% cannot be expected to alter the results by more than that amount. As will be shown below, the difference affected by the use of sodalite far exceeds 3.2%, so the contamination can be assumed to have played a minor role in the results.

### 3.2. Chemical analysis

The samples for Re retention were analyzed by ICP-MS to determine Re concentration in the heated and unheated samples. Mass was lost from the feed as it melted into glass, so a mass-loss correction was determined using the difference in the masses of the original feed and the resulting glass. This correction was applied to the ICP results of the glasses to account for the Re in the original feed. The retention ratio ( $R_i$ ) [25] of the  $i$ -th constituent of a heat-treated sample was calculated with the formula

$$R_i = \frac{g_{i,r}}{g_{i,0}} \quad (1)$$

where  $g_{i,r}$  is the mass fraction measured after melting and  $g_{i,0}$  is the target mass fraction of the  $i$ -th species if it were retained at 100%.

The retention ratios for the AN-102 and A0 samples from the retention test are shown in Table 2. In the case of HLW glass A0,  $R_{\text{Re}} = 89\%$  for Re-sodalite and 74% for  $\text{Re}_2\text{O}_7$ . For low activity glass AN-102,  $R_{\text{Re}} = 48\%$  for Re-sodalite and only 26% for  $\text{Re}_2\text{O}_7$ . The use of sodalite increased the Re-retention as compared to the  $\text{Re}_2\text{O}_7$  test by 20.5% for A0 feed and by 84.9% for AN-102 feed. This increase is presumably due to the fact that sodalite is not volatile and the incorporation of Re in sodalite prevents the Re from volatilizing while the sodalite structure endures.

Fig. 1 shows the retention of Re added as  $\text{Re}_2\text{O}_7$  in A0 glass according to Xu et al. [6]. The fact that the current result shows a 74% retention compared to the ~78% retention at 1150 °C reported by Xu et al. may be due to the much higher levels of Re added in that study (10,000 ppm compared to the 100 ppm used here), but generally agrees well. Note the rapid loss of Re after 1000 °C (Fig. 1); the Re volatility that does occur from A0 happens at very high temperatures, and therefore, the Re/Tc-sodalite must survive to these temperatures to inhibit the volatility of Re/Tc.

As seen in Fig. 1, the temperature at which Re volatility occurred in AN-102 was lower than in A0. In work by Jin et al. [11], Re began to volatilize at 600 °C in AN-102 and retention at 1100 °C was approximately 40% [11]. In Jin et al. [12], the Re retention in AN-102 was 32% at 1100 °C, which is consistent with the current result of 26% retention at 1200 °C, given that the rate of loss was modest above 1000 °C. Most of the Re loss in AN-102 occurred at temperatures <1000 °C. When the loss occurs at lower temperature, this means that the mineral needs to survive at least through those lower temperatures to carry the Re/Tc past the stage of rapid loss. Thus, sodalite had a dramatic effect for increasing the retention in AN-102, although the final retention was lower in AN-102 glass as compared to A0 glass.

Confirmation of the precision of this type of experiment is given in the A0 duplicate samples heated to 1200 °C. The ICP-MS results are shown in Table 3. The experimental error is implied by the ~3% (relative) difference between the duplicates for both  $\text{Re}_2\text{O}_7$  and Re-sodalite samples. The trend shown by Xu et al. is confirmed in the retention for the  $\text{Re}_2\text{O}_7$  at 1200 °C, which is ~60% in Xu et al. [6] (Fig. 1) and here it is reported as 58%. The relative percent difference between  $\text{Re}_2\text{O}_7$  and Re-sodalite is 13.3% at 1200 °C. This is consistent with the explanation that sodalite in A0 decomposes rapidly after 1100 °C while Re volatility increases. The difference in retention between the two sources of Re will be diminished at higher temperatures as the sodalite crystals react with the melt.

### 3.3. Phase analysis

The Re concentrations were so low in the Re-retention samples (100 ppm doped Re) that XRD analysis did not detect any diffraction peaks associated with Re-phases. This was not an unexpected result. For the Re-retention samples, the Re added was meant to be within the range that might be seen in WTP waste and was not meant to be observed by XRD.

In the sodalite durability samples, XRD analysis revealed the decomposition of the sodalite as a function of temperature. In these cases, Re-sodalite was added at much higher levels with the intention that it would be detectable even as it reacted with the glass melt at higher temperatures. These data are shown in Fig. 4, as a normalized fraction of the initial sodalite remaining at various temperatures. The fraction exceeds 1 for several points due to the complexity of the XRD pattern, the in-growth of sodalite in these glasses at various temperatures, and the limitations on being able to accurately quantify each phase. In addition to the many phases present which must be de-convoluted, nosean (a sodalite) is known to form in AN-102 at 600 °C [11], and likely plays a role in the inflated sodalite value at that temperature. Similarly for A0, nosean is known to ingrow over a temperature range from 600 °C to 1000 °C, peaking at 900 °C [26], which correspond to the points in Fig. 4 that are greater than 1. Especially at the lower temperatures, many phases are present and quantifying each is difficult. Because each subsequent temperature is normalized to the lowest, the data shown should be taken to show a qualitative trend in the dissolution of sodalite.

For AN-102 phase analysis samples shown in Fig. 4, 100% of sodalite remained at 800 °C, 50% remained at 1000 °C, and 0% was detected at 1200 °C. The ICP data from Fig. 1 indicate that Re loss in this glass begins at 600 °C and diminishes to a very small rate of loss by 1000 °C. Since the sodalite remained at least partially intact during this duration, it is likely that intact sodalite was able to immobilize Re when it would otherwise be volatilizing.

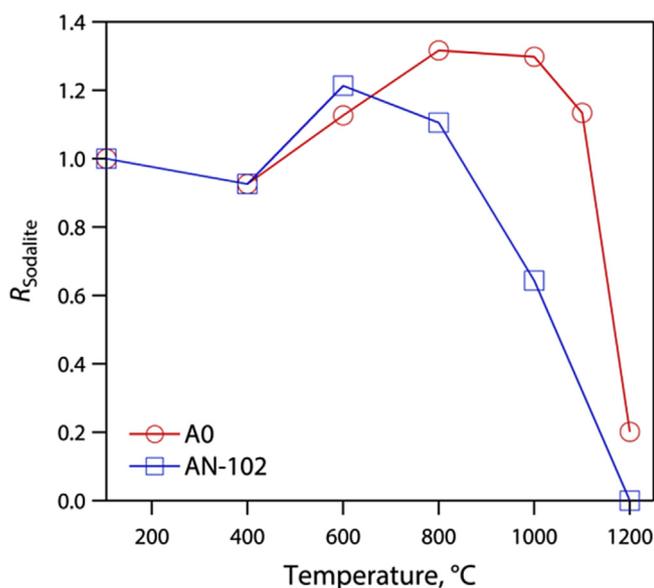
The A0 phase analysis data in Fig. 4 show that sodalite is largely intact below 1100 °C and nearly fully dissolved by 1200 °C. The rhenium loss in A0 occurred mainly above 1100 °C, having only lost 13 mass% of Re by 1100 °C [6]. Since Re was not lost from A0 until

**Table 2**  
Reported Re concentrations and calculated retentions for samples heat treated to 1150 °C.

Glass	Re source	Re concentration (ppm)		Weight-loss factor	Retention	Relative % difference between Re-sodalite and $\text{Re}_2\text{O}_7$ retention
		Pre-heat treatment	Post-heat treatment			
A0	Re-sodalite	73.0	83.7	0.775	0.889	20.5%
	$\text{Re}_2\text{O}_7$	70.4	66.8	0.777	0.738	
AN-102	Re-sodalite	65.8	37.3	0.838	0.475	84.9%
	$\text{Re}_2\text{O}_7$	81.7	25.1	0.836	0.257	

**Table 3**  
Re concentrations and calculated retentions for samples heat treated to 1200 °C in A0 feed.

Re source	Re concentration (ppm)			Weight-loss factor	Retention 1	Retention 2	Average	RPD between Re <sub>2</sub> O <sub>7</sub> and sodalite averages	RPD between heat treatments
	Pre-heat treatment	Post-heat treatment 1	Post-heat treatment 2						
Re-sodalite	101	80.8	83.2	0.808	0.646	0.665	0.656	13.3%	−3.0%
Re <sub>2</sub> O <sub>7</sub>	93.2	67.2	65.5	0.807	0.582	0.575	0.579		2.5%



**Fig. 4.** Sodalite as fraction of original sodalite added in A0 and AN-102 feed-to-glass temperature profile.

the range at which sodalite was breaking down, the durability of sodalite in A0 melts below 1100 °C may be inconsequential, explaining the modest improvement that sodalite had on Re-retention in A0. The durability of sodalite at higher temperatures in A0 may be partially due to the much higher levels of Al in A0 than in AN-102 (see Table 1), which could lower the solubility of the Al from sodalite at lower temperatures. More molten salts in the feed-to-glass transition in AN-102 might contribute to faster sodalite decomposition in that glass.

#### 4. Conclusions

Rhenium retention was increased in both high-level (A0) and low-activity (AN-102) waste glass simulants by using Re-sodalite as a vehicle to inhibit Re volatility. In the case of A0 at 1150 °C, retention was 89% for the Re-sodalite and 74% for Re<sub>2</sub>O<sub>7</sub>, for a 20.5% (relative) improvement when Re-sodalite was used. For low activity glass AN-102, retention was 48% for the Re-sodalite and only 26% for Re<sub>2</sub>O<sub>7</sub>, for an 85% (relative) improvement. Duplicate samples show high precision. Sodalite was shown to be durable in AN-102 glass up to 800 °C and in A0 glass up to 1100 °C. In this study, A0 glass was shown to have much superior Re retention in all cases, but the improvement caused by Re-sodalite in place of Re<sub>2</sub>O<sub>7</sub> was more pronounced in the AN-102 glass. This is due to the temperatures at which sodalite decomposed in the two glasses, and the temperatures at which Re volatility occurred.

Because Tc analogues to Re-sodalite exist, sodalite may be similarly effective at limiting Tc volatility from waste glass melters.

The mechanism of Tc volatility and sodalite decomposition will influence the effectiveness of sodalite as a volatility inhibitor.

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