

UC Davis

UC Davis Previously Published Works

Title

Structure and Thermochemistry of Perrhenate Sodalite and Mixed Guest  
Perrhenate/Pertechnetate Sodalite

Permalink

<https://escholarship.org/uc/item/4cq292zq>

Journal

Environmental Science and Technology, 51(2)

ISSN

0013-936X

Authors

Pierce, Eric M

Lilova, Kristina

Missimer, David M

et al.

Publication Date

2017-01-17

DOI

10.1021/acs.est.6b01879

Peer reviewed

1 **Structure and Thermochemistry of Perrhenate**  
2 **Sodalite and Mixed Guest**  
3 **Perrhenate/Pertechnetate Sodalite**

4 Eric M. Pierce<sup>a\*</sup>, Kristina Lilova<sup>b‡</sup>, David M. Missimer<sup>c</sup>, Wayne W. Lukens<sup>d</sup>, Lili Wu<sup>b</sup>, Jeffrey  
5 Fitts<sup>c</sup>, Claudia Rawn<sup>f</sup>, Ashfia Huq<sup>e</sup>, Donovan N. Leonard<sup>f</sup>, Jeremy R. Eskelsen<sup>a</sup>, Brian F.  
6 Woodfield<sup>h</sup>, Carol M. Jantzen<sup>i</sup>, and Alexandra Navrotsky<sup>b</sup>

7 <sup>a</sup>Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS: 6038,  
8 Oak Ridge, TN 37831

9 <sup>b</sup>Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California at Davis,  
10 Davis, CA 95616

11 <sup>c</sup>Analytical Development Center, Savannah River National Laboratory, Aiken, SC 29808

12 <sup>d</sup>Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

13 <sup>e</sup>Department of Civil & Environmental Engineering, Princeton University, Princeton, NJ 08544

14 <sup>f</sup>Department of Materials Science & Engineering, University of Tennessee, Knoxville, TN 37996

15 <sup>g</sup>Chemical & Engineering Materials Division, Oak Ridge National Laboratory, P.O. Box 2008,  
16 Oak Ridge, TN 37831

17 <sup>h</sup>Chemistry & Biochemistry, Brigham Young University, Provo, UT 84602

18 <sup>i</sup>Environmental Technology Center, Savannah River National Laboratory, Aiken, SC 29808

19  
20 **KEYWORDS**<sup>1</sup>: sodalite, perrhenate sodalite, pertechnetate sodalite, neutron powder diffraction,  
21 x-ray absorption fine structure, high-temperature calorimetry

---

<sup>1</sup> This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

24 **ABSTRACT:** Treatment and immobilization of technetium-99 ( $^{99}\text{Tc}$ ) contained in reprocessed  
25 nuclear waste and present in contaminated subsurface systems represents a major environmental  
26 challenge. One potential approach to managing this highly mobile and long-lived radionuclide is  
27 immobilization into micro- and mesoporous crystalline solids, specifically sodalite. We  
28 synthesized and characterized the structure of perrhenate sodalite,  $\text{Na}_8[\text{AlSiO}_4]_6(\text{ReO}_4)_2$ , and the  
29 structure of a mixed guest perrhenate/pertechnetate sodalite,  $\text{Na}_8[\text{AlSiO}_4]_6(\text{ReO}_4)_{2-x}(\text{TcO}_4)_x$ .  
30 Perrhenate was used as a chemical analogue for pertechnetate. Bulk analyses of each solid  
31 confirm a cubic sodalite-type structure ( $P\bar{4}3n$ , No. 218 space group) with rhenium and  
32 technetium in the 7+ oxidation state. High-resolution nanometer scale characterization  
33 measurements provide first-of-a-kind evidence that the  $\text{ReO}_4^-$  anions are distributed in a periodic  
34 array in the sample, nanoscale clustering is not observed, and the  $\text{ReO}_4^-$  anion occupies the center  
35 of the sodalite  $\beta$ -cage in  $\text{Na}_8[\text{AlSiO}_4]_6(\text{ReO}_4)_2$ . We also demonstrate, for the first time, that the  
36  $\text{TcO}_4^-$  anion can be incorporated into the sodalite structure. Lastly, thermochemistry  
37 measurements for the perrhenate sodalite were used to estimate the thermochemistry of  
38 pertechnetate sodalite based on a relationship between ionic potential and the enthalpy and Gibbs  
39 free energy of formation for previously measured oxyanion-bearing feldspathoid phases. These  
40 results suggest that micro- and mesoporous crystalline solids maybe viable candidates for the  
41 treatment and immobilization of  $^{99}\text{Tc}$ .

## 42 INTRODUCTION

43 Development of a sustainable nuclear fuel cycle, which must include closing the back-end by  
44 recycling and/or disposing of used nuclear fuel, is a key component of the nuclear energy  
45 renaissance (12% of the electrical energy worldwide<sup>1</sup> and 19% in the United States<sup>2</sup>). Disposition  
46 of radioactive waste generated by the nuclear fuel cycle and nuclear weapons production during

47 the Cold War era is one of the most pressing environmental challenges facing the United States  
48 and the international community.<sup>3-4</sup> Furthermore, proposed waste management strategies are  
49 complicated by the inventory of long-lived radionuclides, such as technetium (<sup>99</sup>Tc), and the  
50 time-scales considered for disposal.

51 Since its discovery in 1937 by Perrier and Segre,<sup>5-6</sup> the global inventory of <sup>99</sup>Tc has increased  
52 steadily. Technetium-99 ( $\beta = 293.7$  keV,  $t_{1/2} = 2.1 \times 10^5$  years), a byproduct of <sup>235</sup>U and <sup>239</sup>Pu  
53 fission, comprises a significant component of radioactive waste due to its high fission yield—  
54 ~5%. The world-wide inventory of <sup>99</sup>Tc requiring disposition is estimated to have quadrupled to  
55 ~305 MT from 1994 to 2010 because of nuclear energy production<sup>7</sup> Additionally, US weapons  
56 production sites must dispose of ~5.1 MT of <sup>99</sup>Tc (~3.5 MT at the Savannah River Site and ~1.6  
57 MT at the Hanford Site).<sup>8</sup> Treatment and immobilization of <sup>99</sup>Tc contained in reprocessed nuclear  
58 waste presents a major challenge because <sup>99</sup>Tc volatilizes at the temperatures (~1100 °C) required  
59 for vitrification, the preferred international treatment method.<sup>8-11</sup> The immobilized nuclear waste  
60 glass is destined for long-term storage in a geologic repository.

61 The chemistry of <sup>99</sup>Tc suggests that under aerobic environmental conditions, the stable  
62 heptavalent Tc 7+ pertechnetate anion (<sup>99</sup>TcO<sub>4</sub><sup>-</sup>) is dominant. This oxyanion is soluble and  
63 readily migrates through the environment because it does not adsorb well onto mineral surfaces,  
64 soils, or sediments. Because of the long half-life, abundance, and high environmental mobility of  
65 <sup>99</sup>Tc, incorporating it into durable matrices other than glass is an attractive waste management  
66 strategy.<sup>12</sup> For example, recent studies have examined the possibility of incorporating <sup>99</sup>Tc in the  
67 4+ oxidation state into the structure of iron-based minerals.<sup>13-19</sup> Although various countries are  
68 pursuing vitrification as the primary waste management strategy for other radionuclides (e.g.,  
69 <sup>137</sup>Cs, <sup>90</sup>Sr, U-isotopes, etc.), one approach that has been considered previously but not pursued

70 for disposition and remediation of  $\text{TcO}_4^-$  is encapsulating the radionuclide into micro- and  
71 mesoporous crystalline solids, such as the feldspathoid phase sodalite.

72 Micro- and mesoporous solids represent a family of >150 crystalline phases, which support a  
73 variety of industrial processes (petrochemical cracking, ion exchange for water softening and  
74 purification, and gas separation). These porous materials contribute an estimated \$350 billion to  
75 the global economy as part of the world's chemical industry. The material's structure consists of  
76 a three-dimensional (3D) framework composed of alternative  $\text{TO}_4$  (T = Al or Si) tetrahedral units  
77 covalently joined via oxygen atoms. The 3D framework structure contains a pore or cavity  
78 system that can expand (microporous = 2.5 to 20 Å; mesoporous = 20 to 500 Å) to enclathrate  
79 various guest anions and organic molecules by cooperative changes in the T-O-T bond angle. For  
80 example, aluminosilicate sodalites, both natural and synthetic, can vary widely in composition  
81 but have the general formula of  $\text{M}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{X}_2$ , where M is a monovalent cation (such as  $\text{Cs}^+$ ,  
82  $\text{K}^+$ ,  $\text{Na}^+$ , etc.) and X can vary between monovalent or divalent anions (such as  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  
83  $\text{MnO}_4^{2-}$ ,  $\text{ReO}_4^-$ , or theoretically  $\text{TcO}_4^-$ ).<sup>20-31</sup>

84 Here we use Re as a nonradioactive analogue for  $^{99}\text{Tc}$ , because under oxidizing conditions both  
85 elements are oxyanions and they have similar metal oxygen bond lengths ( $\text{Tc-O} = 1.702$  Å;  $\text{Re-O}$   
86  $= 1.719$  Å) and ionic radii ( $\text{TcO}_4^- = 2.52$  Å;  $\text{ReO}_4^- = 2.60$  Å).<sup>7,32-34</sup> However, under reducing  
87 conditions it is easier to reduce Tc in comparison to Re from 7+ to 4+ because of the difference  
88 in standard reduction potential of  $\text{ReO}_4^-/\text{ReO}_2 = 0.510$  V versus  $\text{TcO}_4^-/\text{TcO}_2 = 0.738$  V.<sup>8,35-36</sup>  
89 Thus, the use of Re as a nonradioactive analogue for  $^{99}\text{Tc}$  is only applicable under oxidizing  
90 conditions where both species are expected to remain in the 7+ oxidation state.

91 Studies by Dickson et al.<sup>37-39</sup> suggest that the  $\text{ReO}_4^-$  anion—and by analogy the  $\text{TcO}_4^-$  anion—  
92 is incorporated into the sodalite  $\beta$ -cage and that anion selectivity for the sodalite  $\beta$ -cage is size-

93 dependent. However, the afore-mentioned studies mainly used changes to the chemical  
94 composition and bulk x-ray powder diffraction spectra to support their conclusions. Although  
95 these results provide key insights on the factors that influence  $\text{ReO}_4^-$  incorporation in to the  
96 sodalite  $\beta$ -cage, they do not provide definitive evidence regarding location of the  $\text{ReO}_4^-$  anion in  
97 the crystalline matrix. As a result, the question of the location and distribution of the  $\text{ReO}_4^-$  anion  
98 remains unanswered. Additionally, the key question of whether or not the  $\text{TcO}_4^-$  anion can be  
99 incorporated into the sodalite structure also remains elusive.

100 In this study, we synthesized and characterized the structure of perrhenate sodalite using, for  
101 the first time, a combination of time-of-flight (TOF) neutron powder diffraction (NPD) and  
102 aberration-corrected high annular angular dark field (HAADF) scanning transmission electron  
103 microscopy (STEM). The TOF-NPD was used to more precisely determine the oxygen positions  
104 and refine structural parameters and the aberration-corrected HAADF STEM was used to  
105 determine the location and distribution of the  $\text{ReO}_4^-$  anion in perrhenate sodalite. Additionally,  
106 we synthesized and characterized the oxidation state of Re and  $^{99}\text{Tc}$  in a mixed guest  
107 perrhenate/pertechnetate sodalite using x-ray absorption spectroscopy, extended x-ray absorption  
108 fine structure, and x-ray powder diffraction. Lastly, calorimetric measurements for the perrhenate  
109 sodalite were used to estimate the thermochemistry of pertechnetate sodalite based on a  
110 relationship between ionic potential and the enthalpy and Gibbs free energy of formation for  
111 previously measured oxyanion-bearing feldspathoid phases.

## 112 **EXPERIMENTAL**

### 113 **Synthesis of Perrhenate Sodalite and Mixed Guest Perrhenate / Pertechnetate Sodalite.**

114 Perrhenate sodalite was synthesized using hydrothermal methods by treating Zeolite 4A with 8M  
115 NaOH in the presence of excess sodium perrhenate at 225°C and 400 psi in an autoclave for 7 d

116 (168 h). The mixed guest perrhenate/pertechnetate sodalite was also prepared hydrothermally  
117 using a similar synthesis approach as above with a 11:1 mole ratio of  $\text{NaReO}_4$  (0.021 moles) to  
118  $\text{NaTcO}_4$  (0.0019 moles). For additional details on the synthesis see the Supporting Information  
119 section.

120 **X-ray Diffraction.** The powder XRD spectrum of the homogenized perrhenate sodalite sample  
121 was measured with a Panalytical X'Pert PRO diffractometer using  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.54060$   
122  $\text{\AA}$ ). Data were collected in  $0.017^\circ$  steps over the  $2\theta$  range  $5\text{--}110^\circ$ . The powder XRD spectrum  
123 for the mixed guest perrhenate/pertechnetate sodalite sample was measured with a Bruker D8  
124 Advance x-ray diffractometer using  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.54060 \text{\AA}$ ). The samples were ground  
125 in an agate mortar and pestle, mixed with a 1:10 collodion/amyl acetate mixture, and smeared  
126 onto a square glass slide. The XRD data were collected in  $0.02^\circ$  step size and a dwell time of 1 s  
127 over the  $2\theta$  range  $5\text{--}70^\circ$ .

128 **X-ray Absorption Spectroscopy.** Rhenium x-ray absorption fine structure (XAFS) analysis  
129 was conducted by placing approximately 200 mg of sample in a Teflon holder sealed with  
130 Kapton tape. The bulk Re  $L_{II}$ -edge (11,959 eV) X-ray Absorption Near Edge Structure (XANES)  
131 spectrum of the perrhenate sodalite was collected in transmission at Stanford Synchrotron  
132 Radiation Lightsource (SSRL) on beamline 11-2. The beamline configuration consisted of a  
133 cryogenically cooled Si(220),  $\phi = 90^\circ$ , double-crystal monochromator with the second crystal  
134 detuned by 70% to reduce the harmonic content of the beam. Incident and transmitted beam  
135 intensity was determined using nitrogen-filled ion chambers. Data were normalized and  
136 corrected for self-absorption using Athena.<sup>40</sup>

137 Technetium XAFS analysis was conducted by mixing 100 mg of mixed Re/Tc sodalite with  
138 100 mg of chloride sodalite and adding the 200 mg mixture to a Teflon holder sealed with

139 Kapton tape. The bulk Tc K-edge (21,047) XANES spectrum of the mixed guest  
140 perrhenate/pertechnetate sodalite was collected in fluorescence at the National Synchrotron Light  
141 Source on beamline X27A with a HPGe detector. Data were averaged using Athena and are not  
142 corrected for detector dead time or self-absorption because neither effect was significant at the  
143 detector count rates and pertechnetate concentrations used in this study (1 mol % pertechnetate in  
144 the mixed guest perrhenate/pertechnetate sodalite).

145 For additional details on the XAS spectrum fitting see Supporting Information.

146 **Neutron Powder Diffraction.** Time-of-flight powder neutron diffraction (PND) data were  
147 collected using 1.312 gram samples of sodium perrhenate [ $\text{Na}_8(\text{AlSiO}_4)_6(\text{ReO}_4)_2$ ] contained in an  
148 8 mm diameter vanadium sample can at 298 K. The PND patterns were collected using the  
149 POWGEN (BL-11A) neutron powder diffractometer at the Spallation Neutron Source (SNS) at  
150 Oak Ridge National Laboratory, Oak Ridge, TN. Diffraction profiles were collected using center  
151 wavelengths 1.066 Å and 2.665 Å, providing a d-spacing range from 0.57 to 6.18 Å. Rietveld  
152 refinements of the data were performed using the GSAS software package along with the  
153 EXPGUI interface.<sup>41-42</sup> The bound coherent scattering lengths  $3.62 \pm 0.02$  fermi (fm) for sodium,  
154  $3.449 \pm 0.005$  fm for aluminum,  $4.149 \pm 0.001$  fm for silicon,  $9.2 \pm 0.2$  fm for rhenium, and  
155  $5.803 \pm 0.004$  fm for oxygen. The large bound coherent scattering length of oxygen allows the  
156 oxygen positions to be determined using neutron diffraction with more accuracy than with XRD.  
157 Additionally, the difference in the bound scattering length for the aluminum, rhenium, and  
158 silicon atoms allows these elements to be distinguished better using neutron powder diffraction  
159 than with XRD. The atomic structure for  $\text{Na}_8(\text{AlSiO}_4)_6(\text{ReO}_4)_2$  previously reported was used as  
160 the starting model for calculating the diffraction patterns.<sup>29-30</sup>



161 **Microscopy imaging.** Atomic resolution aberration-corrected STEM images were obtained  
162 with a Nion Ultra STEM 60-100 electron microscope. This was equipped with a cold field  
163 emission gun and operated at 100kV with a 3<sup>rd</sup> generation C3/C5 aberration corrector. The  
164 aberration-corrected HAADF STEM images were performed with a probe current of 80 pA.  
165 Beam damage was readily apparent when imaging in the STEM (see Fig. SI2) and electron dose  
166 was minimized by using fast scan speeds at the largest field of view that atomic columns could  
167 still be resolved. Perrhenate sodalite powder was suspended in 50 mL of IPA and a 10  $\mu$ L droplet  
168 was cast onto a 3mm copper lacey carbon TEM grid and the solution was allowed to evaporate.  
169 The drop cast TEM grid was then prebaked in a vacuum oven station at 160°C for 8 hours in a  
170 vacuum at  $\sim 10^{-6}$  torr and then allowed to cool under vacuum for 10 hours. STEM imaging was  
171 performed on a single grain of perrhenate sodalite that was positioned on the lacey carbon in a  
172 crystallographic orientation close to [111] zone axis. STEM stage tilts were then used to properly  
173 orient the sample into a [111] zone axis for atomic column resolution imaging. The [111] zone  
174 axis was selected because it was ideal for observing the  $\text{ReO}_4^-$  anion present inside the sodalite  $\beta$ -  
175 cage. Details of the scanning electron microscopy (SEM) and energy dispersive spectroscopy  
176 (EDS) measurements for both the perrhenate sodalite and mixed perrhenate/pertechnetate  
177 sodalite are provided in the Supporting Information.

178 **Calorimetry.** High temperature oxide melt solution calorimetry was performed using a Tian  
179 Calvet twin calorimeter described in detail by Navrotsky.<sup>43-44</sup> In the drop solution calorimetry  
180 experiment, samples in the form of pellets (between 4 and 6 mg) were dropped from room  
181 temperature (298 K) into the molten  $2\text{PbO}\cdot\text{B}_2\text{O}_3$  at the calorimeter temperature in a platinum  
182 crucible. Air was flushed over the solvent at 90 ml/min. The calorimeters were calibrated using  
183 the heat content of 5 mg  $\alpha\text{-Al}_2\text{O}_3$  pellets.

184 A preliminary furnace test was performed before conducting the calorimetry measurements to  
185 verify the complete dissolution of the sample. Pellets of approximately 5 mg were prepared and  
186 dropped in molten lead borate solvent ( $2\text{PbO}\cdot\text{B}_2\text{O}_3$ ), maintained at 973 K in a furnace. The  
187 dissolution process started immediately and finished in a minute. After quenching the melt, no  
188 undissolved material was found.

## 189 **RESULTS AND DISCUSSION**

190 **Synthesis and Characterization of Perrhenate Sodalite.** The hydrothermal reaction  
191 produced a crystalline powder with perrhenate sodalite particles that ranged from 0.5 to 5  $\mu\text{m}$  for  
192 individual crystals (Fig. S11) and agglomerated crystals 10  $\mu\text{m}$  or less. The chemical composition  
193 was within the experimental error of what is expected for a stoichiometric sample (see Table S1).

194 To confirm the bulk rhenium oxidation state following hydrothermal synthesis, X-ray  
195 absorption near-edge spectroscopy (XANES) was performed on the resulting solid. The Re  $L_2$ -  
196 edge XANES spectra of the four standards are shown in Fig. S13.<sup>35</sup> Two major changes are  
197 observed in the rhenium standard reference spectra as one proceeds from Re metal (Re [0]  
198 oxidation state) to  $\text{ReO}_4^-$  (Re [7+] oxidation state). First, the absorption edge shifts to higher  
199 energy because the binding energy of the electron increases as the formal oxidation state  
200 increases; there are fewer electrons to screen the charge of the nucleus from the 2p electrons.  
201 Second, the area of the large peak at the absorption edge—the “white line,” which is associated  
202 with the 2p to 5d transition—increases as the rhenium oxidation state increases because the area  
203 is proportional to the number of vacancies in the 5d orbitals (Fig. S13). Analysis of the  
204 perrhenate sodalite XANES spectrum indicates that only  $\text{ReO}_4^-$  is present (Fig. S13) but the fit  
205 using the standard reference spectrum suggests that  $\text{KReO}_4$  is less than optimal (Table S12). The

206 discrepancy is due to the difference between the local environments of  $\text{ReO}_4^-$  in perrhenate  
207 sodalite and  $\text{KReO}_4$ , as discussed below.

208 In addition to these major differences, the XANES region just above the edge contains features  
209 due to extended x-ray absorption fine structure (EXAFS), especially those caused by multiple  
210 scattering. The major changes are clearly seen in Fig. SI3 as the spectrum from standard  
211 compounds transition through the range of oxidation states from the 4+ ( $\text{ReO}_2$ ) to 7+ ( $\text{KReO}_4$ ).  
212 The smaller EXAFS contributions may be seen in the size and spacing of the features at energies  
213 above that of the white line. As noted above, the EXAFS contributions result in slightly different  
214 spectra for  $\text{KReO}_4$  versus perrhenate sodalite. Although both materials contain the tetrahedral  
215 coordinated  $\text{ReO}_4^-$  anion, in the  $\text{KReO}_4$ , the potassium ion interacts strongly with the  $\text{ReO}_4^-$  anion  
216 (the only anion present in  $\text{ReO}_4^-$ ); in perrhenate sodalite, the sodium ions interact with both the  
217 negatively charged sodalite framework and the  $\text{ReO}_4^-$  anion. The resulting weakening of the  
218 interaction between  $\text{ReO}_4^-$  and the sodium ions is reflected in the decrease of the Re–O bond  
219 distance in perrhenate sodalite, 1.729(7) Å, versus  $\text{NaReO}_4$ , 1.728(2) Å,<sup>45</sup> and in  $\text{KReO}_4$ ,  
220 1.723(4) Å<sup>46-47</sup> (Fig. 1 and Table SI3). The observed shortening of the Re–O bond length in the  
221 sodalite crystal structure is consistent with the shortening of the Mn–O bond length in  
222 permanganate sodalite.<sup>31,48</sup>

223  
224

225 **Fig. 1.** Extended Re  $L_2$ -edge EXAFS spectrum of perrhenate sodalite,  $\text{Na}_8[\text{AlSiO}_4]_6(\text{ReO}_4)_2$ . The  
226 EXAFS data and fit are depicted as a solid gray line and black circles, respectively. Fit range:  $2 <$   
227  $k < 11$  (a);  $0.8 < R < 2.0$  (b); the number of independent points was 8.6, and the number of  
228 parameters was 4.

Wayne Lukens User 10/31/2017 9:53 AM

Deleted: Fig. 1

230 A combination of powder x-ray diffraction (pXRD) (not shown) and neutron powder  
231 diffraction (NPD) (**Fig. 2**) measurements were performed on the perhenate sodalite sample. The  
232 crystallography data are provided in **Table 1**. The refined atomic positions, site occupancies, and  
233 atomic displacement parameters are given in Table SI4 for the NPD results. It was possible to  
234 refine the anisotropic displacement parameters for all of the atoms with the exception of  
235 aluminum with the NPD results (see Table SI5). For the aluminum atom, the atomic  
236 displacement parameter was ~5 times smaller than the silicon atom; one explanation for this  
237 difference is that portion of the aluminum sites have been replaced by silicon atoms, which has a  
238 smaller neutron cross-section. The data was subsequently refined with the aluminum site  
239 occupied by both aluminum and silicon atoms, which resulted in site occupancies of 83(7)%  
240 aluminum and 17(7)% silicon. The refined value of  $U_{\text{iso}}$  only slightly increased to  $0.47(9) \times 100$ ,  
241 and the  $\chi^2$  decreased slightly to 2.109. The formula obtained by refining the site occupancy of the  
242 oxygen atom, labeled as O2 in Table SI4 – SI6, is  $\text{Na}_8(\text{AlSiO}_4)_6(\text{ReO}_{3.75})_2$ , compared with  
243  $\text{Na}_8(\text{Al}_{0.83}\text{Si}_{1.17}\text{O}_4)_6(\text{ReO}_{3.75})_2$  when the aluminum site is shared by both aluminum and silicon.  
244 Similar to the NPD, the pXRD results indicate a sodalite-type structure with a  $P\bar{4}3n$  (No. 218)  
245 space group and lattice parameter  $a = 9.15283(8) \text{ \AA}$  (Table SI6). These bulk measurements are  
246 consistent with the results obtained previously by Mattigod and colleagues.<sup>29-30</sup>

247

248

249 **Fig. 2.** Rietveld refinement profiles of powder neutron diffraction data for perhenate sodalite,  
250  $\text{Na}_8[\text{AlSiO}_4]_6(\text{ReO}_4)_2$ . The neutron diffraction data were collected using two different center  
251 wavelengths to access different d-spacing ranges (d-spacing from 0.5 to  $3.0 \text{ \AA}$  on [a] and d-  
252 spacing from 1.1 to  $6.2 \text{ \AA}$  [b]).

Wayne Lukens User 10/31/2017 9:53 AM

Deleted: Fig. 2

Wayne Lukens User 10/31/2017 9:53 AM

Deleted: Table 1