FINAL REPORT
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Technetium (VII) Co-precipitation with Framework Aluminosilicates

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Abstract

Technetium-99 (^{99}Tc), a long-lived radionuclide, is one of the most widespread contaminants within the Hanford subsurface. At some depths, it is only extractable with strong acids, suggesting incorporation into a solid phase. We hypothesized that Tc may have coprecipitated with feldspathoid aluminosilicates under waste tanks that had leaked caustic solutions into the vadose zone. Our objectives were to determine if Tc could be incorporated into the feldspathoids cancrinite and sodalite and under what conditions coprecipitation could occur. Our hypothesis was that sodalite was more likely to incorporate and retain Tc. Our approach was to use known methods of feldspathoid formation in solutions resembling those in Hanford waste tanks contacting sediments in terms of major ion (Na, NO_3, OH, $Al(OH)_4$, and $Si(OH)_4$ concentrations. In some cases, Al and Si were supplied from zeolite. We used perrhenate (ReO_4) as a surrogate for pertechnetate (TcO_4) to avoid the radioactivity. The major findings of this study were 1) ReO_4 could be incorporated into either sodalite or cancrinite but the concentration in the solid was < 1% of the competing ion Cl, NO_3, or NO_2. 2) The small amount of ReO_4 incorporated was not exchangeable with NO_3 or NO_2. 3) In sodalite, NO_3 was highly preferred over ReO_4 but significant Re-sodalite was formed when the mole fraction in solution (Re/Re+N) exceeded 0.8. 4) A nonlinear relation between the unit cell parameter and amount of Re incorporated suggested that a separate Re-sodalite phase was formed rather than a solid solution. 5) We determined that sodalite preference for sodalite in the presence of different anions increased with the ionic size of the competing anion: $Cl < CO_3 < NO_3 < SO_4 < MnO_4 < WO_4$ and significant incorporation did not occur unless the difference in anion radii was less than 12%. 6) Re(VII) was not significantly reduced to Re(IV) under the conditions of this experiment and Re appeared to be a good surrogate for Tc under oxidizing conditions as both oxyanions have the same size. In conclusion, incorporation of TcO_4 is unlikely in the close proximity to the tanks where sodalite is likely to form in the presence of high NO_3 and other anions much smaller than TcO_4.

ACKNOWLEDGEMENTS

This work was carried out by Dr. John Dickson as part of his PhD dissertation at Washington State University under the guidance of Dr. James Harsh (WSU, advisor), Dr. Eric Pierce (ORNL, co-advisor) and Dr. Markus Flury (WSU, committee member). Dr. Dickson was first author on three peer-reviewed manuscripts from this work.

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Introduction

This report stems from work started in 2010 and concluded in January, 2015 when Dr. John Dickson completed his final manuscript for publication and left Washington State University for a postdoctoral research position at ORNL. DOE funding for the project covered the period from September, 2010 to September, 2012. In the report we will state the motivation for the work, the initial objectives of the project, and the major findings and implications. Substantiated findings, their implications, and the author's (Harsh) opinions are contained in the Conclusions section and a more detailed presentation of the problem, results, conclusions, and recommendations follows in the summary. The end of the report consists of a list of presentations and publications from the work.

We are grateful to the Department of Energy Office of Science for the chance to carry out this work and sincerely hope that our results are helpful in determining remediation strategies for the Hanford Site cleanup efforts.

Conclusions

The major findings of this study were 1) ReO_4 could be incorporated into either sodalite or cancrinite but the concentration in the solid was < 1% of the competing ion Cl, NO_3, or NO_2. 2) The small amount of ReO_4 incorporated was not exchangeable with NO_3 or NO_2. 3) In sodalite, NO_3 was highly preferred over ReO_4 but significant Re-sodalite was formed when the mole fraction in solution (Re/Re+N) exceeded 0.8. 4) A nonlinear relation between the unit cell parameter and amount of Re incorporated suggested that a separate Re-sodalite phase was formed rather than a solid solution. 5) We determined that sodalite preference for sodalite in the presence of different anions increased with the ionic size of the competing anion: Cl $< CO_3 < NO_3 < SO_4 < MnO_4 < WO_4$ and significant incorporation did not occur unless the difference in anion radii was less than 12%. 6) Re(VII) was not significantly reduced to Re(IV) under the conditions of this experiment and Re appeared to be a good surrogate for Tc under oxidizing conditions as both oxyanions have the same size. In conclusion, incorporation of TcO_4 is unlikely in the close proximity to the tanks where sodalite is likely to form in the presence of high NO_3 and other anions much smaller than TcO_4.

One limitation of our results is that sodalite synthesis occurred in a closed system. In open, free-flowing systems such as the subsurface, the smaller anions may become depleted leaving TcO_4 to be incorporated later in the reaction sequence. Additionally, our experiments were designed specifically to form only sodalite phases because of the ability of its cages to sequester large ions such as TcO_4. In other systems, neoformed mineral phases could include cancrinite, zeolite, nosean, and nepheline. It has been reported that NO_3 is preferentially sequestered by cancrinite and SO_4 by nosean, whereas Cl and ReO_4 are incorporated into mixed-anion sodalites (Pierce et al., 2014). Thus, at the comparatively low concentrations of TcO_4 (10^{-6} to 10^{-4} *M*) expected in most nuclear waste streams, TcO_4 could intercalate into the mixed-anion sodalite phases after other competing anions have been selectively sequestered into their respective neoformed mineral phases.

Lastly, a nuclear waste reprocessing scheme that removes NO_3 and NO_2, such as the fluidized bed steam reformer process, could be used to decrease the concentration of competing anions and enhance ReO_4 (and ultimately TcO_4) sequestration into a nuclear waste form comprised of mixed-anion sodalites (Pierce et al., 2014a).

Further work is needed in open systems, with a greater range of conditions (temperature and dynamic flow synthesis of an array of aluminosilicate mineral phases), and at realistic 99Tc concentrations, to mimic waste-impacted subsurface sediments and managed reprocessed nuclear waste streams to determine if mixed-anion sodalites may be relevant sequestering phase(s).

Summary

The project was motivated by the finding that ^{99}Tc leaked from Hanford waste tanks was retained by sediments under the tanks in a form that required strong acid dissolution to extract. This finding contrasted with the predicted chemistry of Tc in the environment under the tanks where Tc is expected to occur as the pertechnetate (TcO_4) anion. Pertechnetate is not known to adsorb strongly to sediments at the Hanford site suggesting that it was incorporated into an acid soluble solid phase. Previous research focused on ^{90}Sr and ^{137}Cs demonstrated that these elements are incorporated into a feldspathoid phase (e.g., sodalite [$Na_8(Al_6Si_6O_{24})Cl_2$], cancrinite [$Na_8Al_6Si_6O_{24}SO_4 \bullet 2H_2O$], or zeolite intermediate) that formed as a result of the contact between Hanford sediments and the HLW solutions. Additionally, it was been shown the perrhenate anion (as ReO_4), a chemical analogue for TcO_4^-, can be incorporated into feldspathoid minerals (e.g., sodalite, cancrinite, and nosean [$Na_8[Al_6Si_6O_{24}]SO_4$]) by substituting for the central anion (e.g, NO_3, Cl or SO_4) in the structure (Fig. 1). Our overarching hypothesis was that TcO_4 could be incorporated into the feldspathoids as they precipitated below Hanford waste tanks.

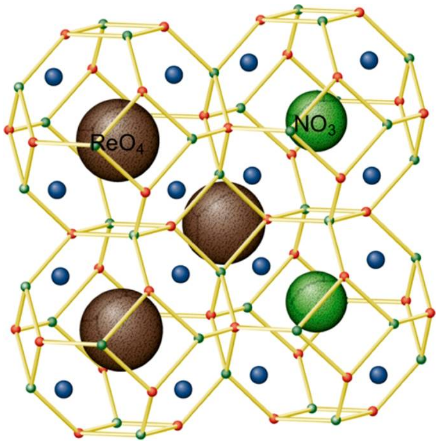

Figure 1. Model of oxyanions occupying sodalite cages in NO_3/ReO_4-sodalite

The initial project objectives were to **(1)** identify and characterize pertechnetate-containing feldspathoid phases present in contaminated Hanford sediment, **(2)** identify the microbial community present in these contaminated sediments, **(3)** synthesize ^{99}Tc-containing feldspathoids phases in the presence and absence of Hanford sediments, **(4)** quantify the biotic effects of microbial activity on ^{99}Tc-containing feldspathoids, and **(5)** quantify the effect abiotic changes in the microenvironments will have on ^{99}Tc anion substitution and feldspathoid phase dissolution. Because this proposal was funded as a two-year exploratory project, we focused on Objective 2, the synthesis and characterization of feldspathoids formed in the presence of ReO_4, an analog of TcO_4. These two anions are nearly identical in terms of ion size and charge, differing only in oxidation potential. Our hypothesis considered only the Tc(VII) and Re(VII) oxidation states, which are the most stable under conditions found below the Hanford tanks. We used x-ray diffraction, chemical analysis, microscopic characterization, and x-ray absorption to characterize the materials and assess the type and extent of ReO_4 incorporation into sodalite and cancrinite and ion exchange to determine the susceptibility to removal from the solids. The results obtained from these experiments will provide some of the fundamental data needed to conduct future projections on ^{99}Tc migration in the subsurface.

The first set of experiments were designed to test the hypothesis that ReO_4 could be coprecipitated with either cancrinite or sodalite and that the oxyanion, once incorporated would be nonexchangeable (Dickson et al., 2015a). We investigated the incorporation of ReO_4 precipitated in the presence of competing anions (X) including OH, NO_2, NO_3, and Cl and under conditions mimicking tank waste solution compositions. The resulting solids were characterized by their chemical composition, structure, and morphology. Regardless of solution pH, sodalite formed in the presence of Cl and NO_2 whereas NO_3 promoted either cancrinite formation in 16-mol OH^-/kg (16 m) or mixed sodalite/cancrinite phases in 1-mol OH^-/kg (1 m) solutions. In the presence of Cl, NO_2, and NO_3 less than 0.02 mol fraction of ReO_4 was incorporated into the feldspathoid phase(s) (Fig. 2). Although, the NO_2 sodalite and mixed NO_3 cancrinite/sodalite phases incorporated significantly more ReO_4 than NO_3 cancrinite or Cl-sodalite phases, the total ReO_4 fraction was ~1% or less of the total sites. The ReO_4 immobilized in ReO_4-sodalite, NO_2-sodalite, mixed NO_3-cancrinite/sodalite and NO_3-cancrinite was resistant to ion exchange with either NO_2 or NO_3. The results imply that ReO_4, and thus by analogy $^{99}TcO_4$, does not compete well with smaller ions for

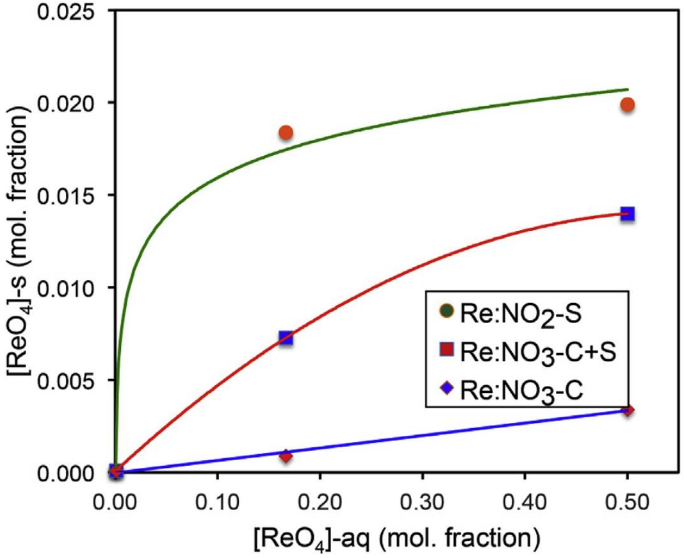

Figure 2. Variation of ReO_4 sequestered in feldspathoids with ReO_4 solution mole fraction.

Table 1. Exchangeability of ReO_4 with NO_2 or NO_3.

Solution ReO_4^- after aqueous exchange of feldspathoids with NO_2^- or NO_3^-.

Feldspathoid type	ReO_4^- in feldspathoids (mmol/kg)	Solution ReO_4^- following 96 h of suspension (mmol/kg)	(%)
Re:NO_3–C-2[b]	2.81 ± 0.16	0.01	0.36
Re:NO_3–C + S-2[b]	6.91 ± 0.13	0.02	0.29
Re:NO_2–S-2[a]	16.67 ± 0.15	0.04	0.24
ReO_4-Sodalite[b]	1388.80 ± 17.72	3.05 ± 0.03	0.22

[a] Exchange with 0.1 *M* NO_2^- solution.

[b] Exchange with 0.1 *M* NO_3^- solution.

incorporation into feldspathoids, but, once sequestered, is difficult to exchange. Because ReO_4 is a suitable surrogate for $^{99}TcO_4$ under oxidizing conditions, our results suggest that sodalite can sequester $^{99}TcO_4$, but the presence of smaller competing anions at similar or higher concentrations may preclude its incorporation during mineral formation. In an open system such as a waste stream that leaked into vadose zone sediments, other mineral phases such as zeolite, nosean, nepheline may form that have a higher affinity for larger anions. For example, Pierce et al. (2014) showed that NO_3 will incorporate into cancrinite and SO_4 into nosean; whereas Cl, NO_2 and ReO_4 will be intercalated into sodalite. In a dynamic, open system, TcO_4 could be sequestered into the sodalite phases after other small competing anions have been selectively removed by earlier-forming phases, including sodalite. Additionally, a waste-reprocessing scheme (e.g., the fluidized bed steam reformer process) that reduces NO_3 and NO_2 could be used to enhance ReO_4 (and ultimately TcO_4) sequestration into mixed-anion feldspathoids.

The second part of the study focused on the formation of mixed NO_3/ReO_4-sodalites (Dickson et al., 2014). Mixed-anion sodalites were hydrothermally synthesized in the laboratory from zeolite A in sodium hydroxide, nitrate, and perrhenate solutions at 90°C for 24 h. The resulting solids were characterized by bulk chemical analysis, X-ray diffraction, scanning electron microscopy, and X-ray absorption near edge structure spectroscopy (XANES) to determine the products' chemical composition, structure, morphology, and Re oxidation state. The XANES data indicated that nearly all rhenium (Re) was incorporated as Re(VII)O_4. The nonlinear increase of the unit cell parameter with ReO_4/NO_3 ratio suggests formation of two separate sodalite phases in lieu of a mixed-anion sodalite (Fig. 3).

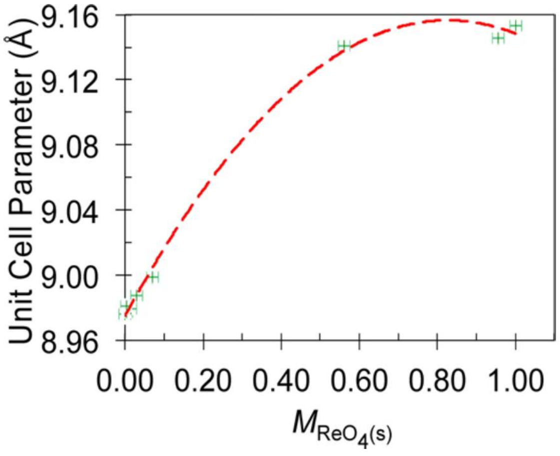

Figure 3. Dependence of the unit cell parameter on ReO_4–concentration in ReO_4/NO_3-sodalite.

The results reveal that the sodalite cage is highly selective toward NO_3 over ReO_4 (Fig. 4). Calculated enthalpy and Gibbs free energy of formation at 298 K for NO_3 and ReO_4 sodalite suggest that NO_3 incorporation into the cage is favored over the incorporation of the larger ReO_4 due to the smaller ionic radius of NO_3. Based on these results, it is expected that NO_3, which is present at significantly higher concentrations in alkaline waste solutions than $^{99}TcO_4$, will be strongly preferred for incorporation into the sodalite cage.

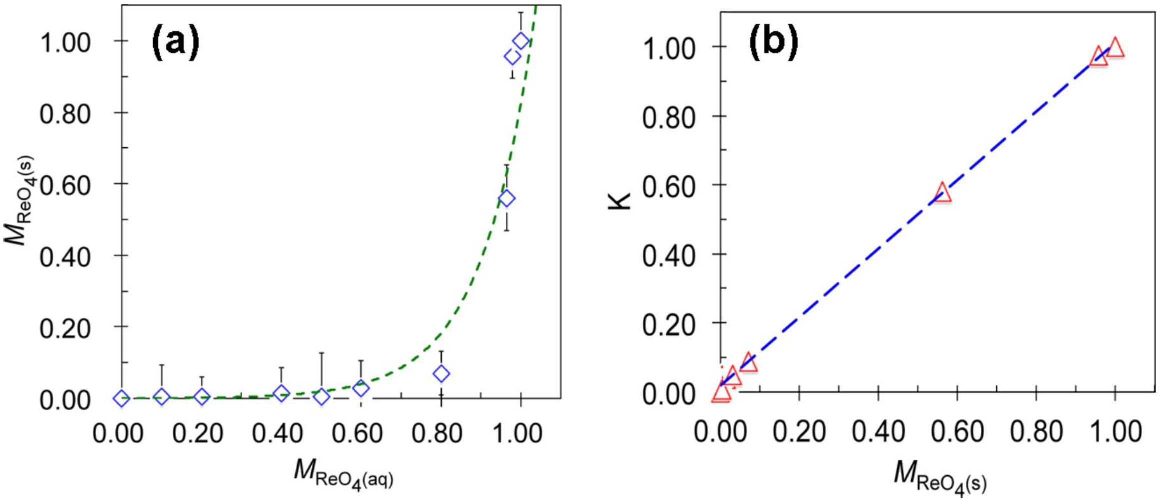

Figure 4. (a) Selectivity graph for rhenium incorporation into ReO_4/NO_3-sodalite; generally more than 90% of sodalite cages are filled with oxyanions. (b) Selectivity coefficient (K_{Re}/N) as a function of ReO_4 mole fraction in the mixed sodalite $(M_{ReO_4(s)})$.

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Given the low selectivity of ReO_4 for incorporation into feldspathoids relative to the smaller anions Cl, NO_2, and NO_3, a study to determine the role of anion size on sodalite composition was undertaken (Dickson et al., 2015b). Perrhenate, as a TcO_4 analogue, was incorporated into mixed-anion sodalites from binary solutions containing ReO_4 and a competing anion Xn (Cl, CO_3, SO_4, MnO_4, or WO_4). Our objective was to determine the extent of solid solution formation and the dependence of competing ion selectivity on ion size. Using equivalent aqueous concentrations of the anions (ReO_4/X molar ratio = 1:1), we synthesized mixed-anion sodalites from zeolite and NaOH at 90°C for 96 h. The resulting solids were characterized by bulk chemical analysis, powder X-ray diffraction, scanning electron microscopy, and X-ray absorption near edge structure (XANES) spectroscopy to determine crystal structure, chemical composition, morphology, and rhenium (Re) oxidation state. Rhenium in the solid phase occurred predominately as $Re(VII)O_4$.

Five mixed-anion sodalites containing extra- framework species were synthesized and characterized. The selectivity for intra-lattice anions of the products was highly dependent on the size and, to a lesser extent, the charge of the competing anion. The results of our study suggest that similarity in ionic radius (DIR of ≤ 15%) and charge (ionic potential) promote the competitive incorporation of ReO_4 into the mixed-anion sodalites. Selectivity of ReO_4 for the mixed-anion sodalites was found to increase in the series as follows: Cl < CO_3 < NO_3 < SO_4 < MnO_4 < WO_4 (Fig. 5).

The findings in this study have implications for the fate and transport of $^{99}TcO_4$ in subsurface sediments, assuming that its chemical behavior can be well approximated by ReO_4. Firstly, the formation of a ReO_4/MnO_4-sodalite solid solution implies that ReO_4 is a suitable analogue for TcO_4. Like TcO_4, MnO_4 shares a similar size, and ionic potential with ReO_4.

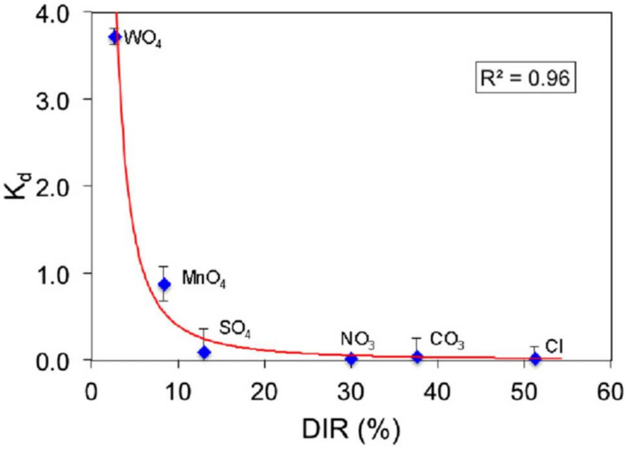

Figure 5. . The distribution coefficient (Kd) graph for ReO_4 sequestered in mixed-anion sodalites as a function of the DIR. Generally, more than 90% of sodalite cages are filled with anions.

The distribution coefficient for ReO_4 was unity, implying nearly equal selectivity for MnO_4 and ReO_4 during the formation of sodalite. The same is likely true for TcO_4 sodalite.

Secondly, our results also suggest that while neoformed feldspathoid minerals, such as sodalite, can incorporate ^{99}Tc as TcO_4, smaller competing anions with DIR > 12% will be preferred. Unfortunately, in many instances where subsurface sediments have been exposed to high-level tank waste and conditions are conducive for feldspathoid formation, the tank waste solutions also contain a high concentration of competing anions.

Products

Presentations:

Harsh J.B.; Pierce E. M.; Dickson J. O.; Peyton B.; Wellman D.; and Bargar J., (2011). Potential for Alumino-silicate Minerals to Control the Availability of Technetium in 200 Area Sediments., DOE ERSP Annual PI Meeting Abstracts

Pierce E. M.; Harsh J. B.; and Dickson J. O., (2011). The Structure and Lability of Re(VII)-sodalite. Goldschmidt Annual Meeting Abstracts. Prague, Czech Republic

Harsh J. B., Dickson J. O., and Pierce E. M., (2012). Sequestration of perrhenate by Sodalite. Goldschmidt Annual Meeting Abstracts. Montreal, Quebec, Canada

Dickson J. O., Harsh J. B., and Pierce E. M., (2012). Sequestration of Perrhenate—a ^{99}Tc-analog—by Sodalite. ASA-CSSA-SSSA Annual conference Abstracts/Poster. Cincinnati, Ohio

Dickson J. O., Harsh J. B., and Pierce E. M., (2014). Sequestration of Perrhenate—a ^{99}Tc-analog—by Sodalite in competition with Nitrate. ACS Annual conference Abstracts/Poster, Dallas, Texas

Dickson J. O., Harsh J. B., and Pierce E. M., (2014). Hydrothermal Synthesis and Structural Characterization of Mixed Anion Sodalite. Goldschmidt Annual Meeting Abstracts/posters, Sacramento, California

Publications:

Dickson, J.O., Harsh, J.B., Flury, M., Lukens, W.W., Pierce, E.M., 2014. Competitive Incorporation of Perrhenate and Nitrate into Sodalite. Environmental Science & Technology 48, 12851-12857.

Dickson, J.O., Harsh, J.B., Flury, M., Pierce, E.M., 2015a. Immobilization and exchange of perrhenate in sodalite and cancrinite. Microporous and Mesoporous Materials 214, 115-120.

Dickson, J.O., Harsh, J.B., Lukens, W.W., Pierce, E.M., 2015b. Perrhenate incorporation into binary mixed sodalites: The role of anion size and implications for technetium-99 sequestration. Chemical Geology 395, 138-143.

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Pierce, E.M., Lukens, W.W., Fitts, J.P., Jantzen, C.M., Tang, G., 2014. Experimental determination of the speciation, partitioning, and release of perrhenate as a chemical surrogate for pertechnetate from a sodalite-bearing multiphase ceramic waste form. Applied Geochemistry 42, 47-59.

Pierce, E.M., Lilova, K., Lukens, W.W., Navrotsky, A., Fritts, J., Rawn, C., Jantzen, C.M.,Missimer, D.M., Huq, A. (Submitted). Structure and thermochemistry of perrhenate sodalite and perrhenate/pertechnetate guest–guest sodalite. Proc. Natl. Acad. Sci. U. S. A.