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Thermodynamics of Hydrothermal Uranyl Mineral Formation at Nopal I

William M. Murphy
California State University, Chico
Department of Geological and Environmental Sciences

James D. Prikryl and David A. Pickett
Center for Nuclear Waste Regulatory Analyses (CNWRA)
Geosciences and Engineering Division
Southwest Research Institute®, San Antonio, Texas

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Alteration of Uraninite to Hydrous Uranyl Minerals in Silicified Tuff {4 cm [1.6 in] Across}

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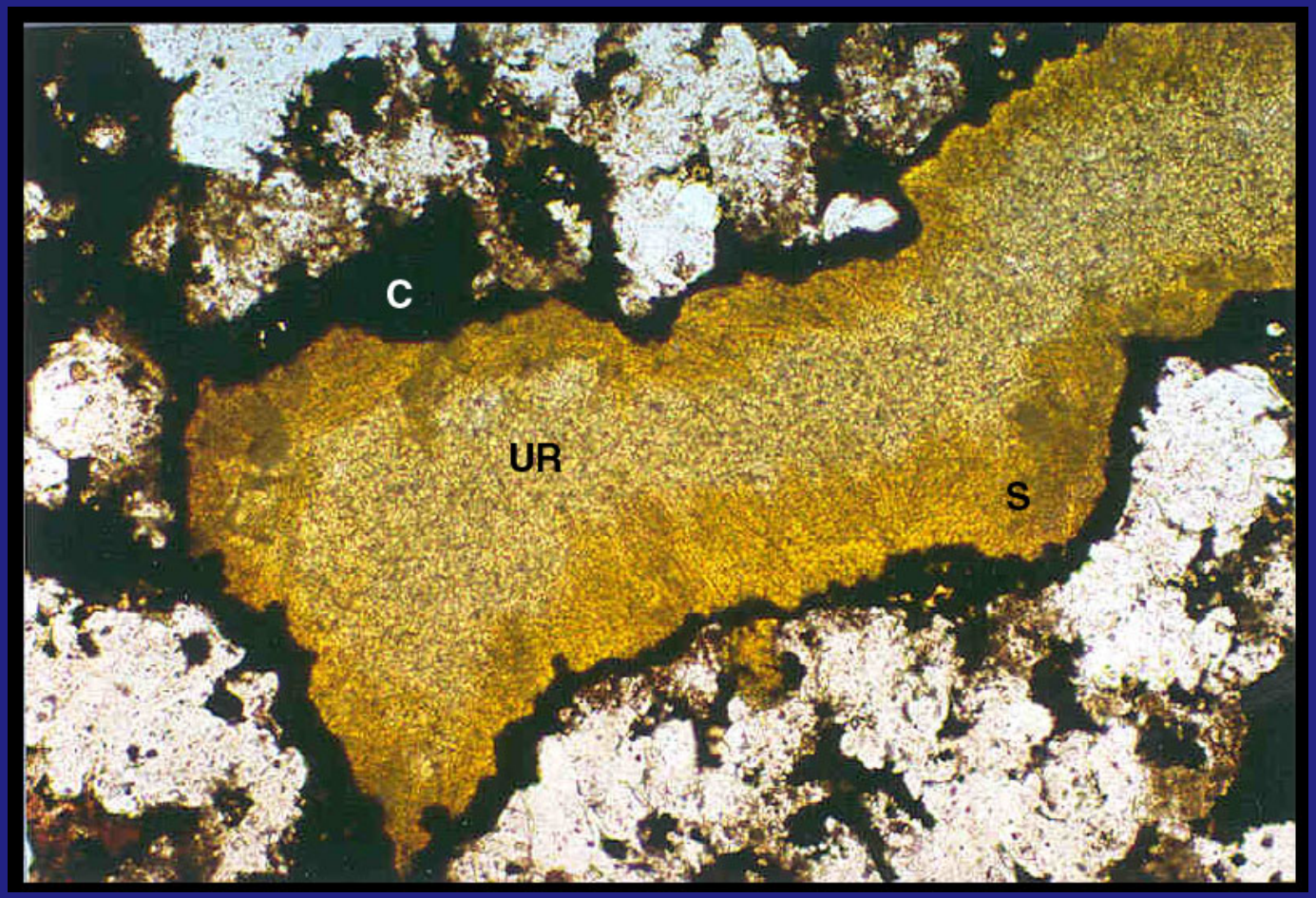
Colloform Uraninite (C) Succeeded by Schoepite (S) and Uranophane (UR)

{0.8 mm [0.03 in] across}



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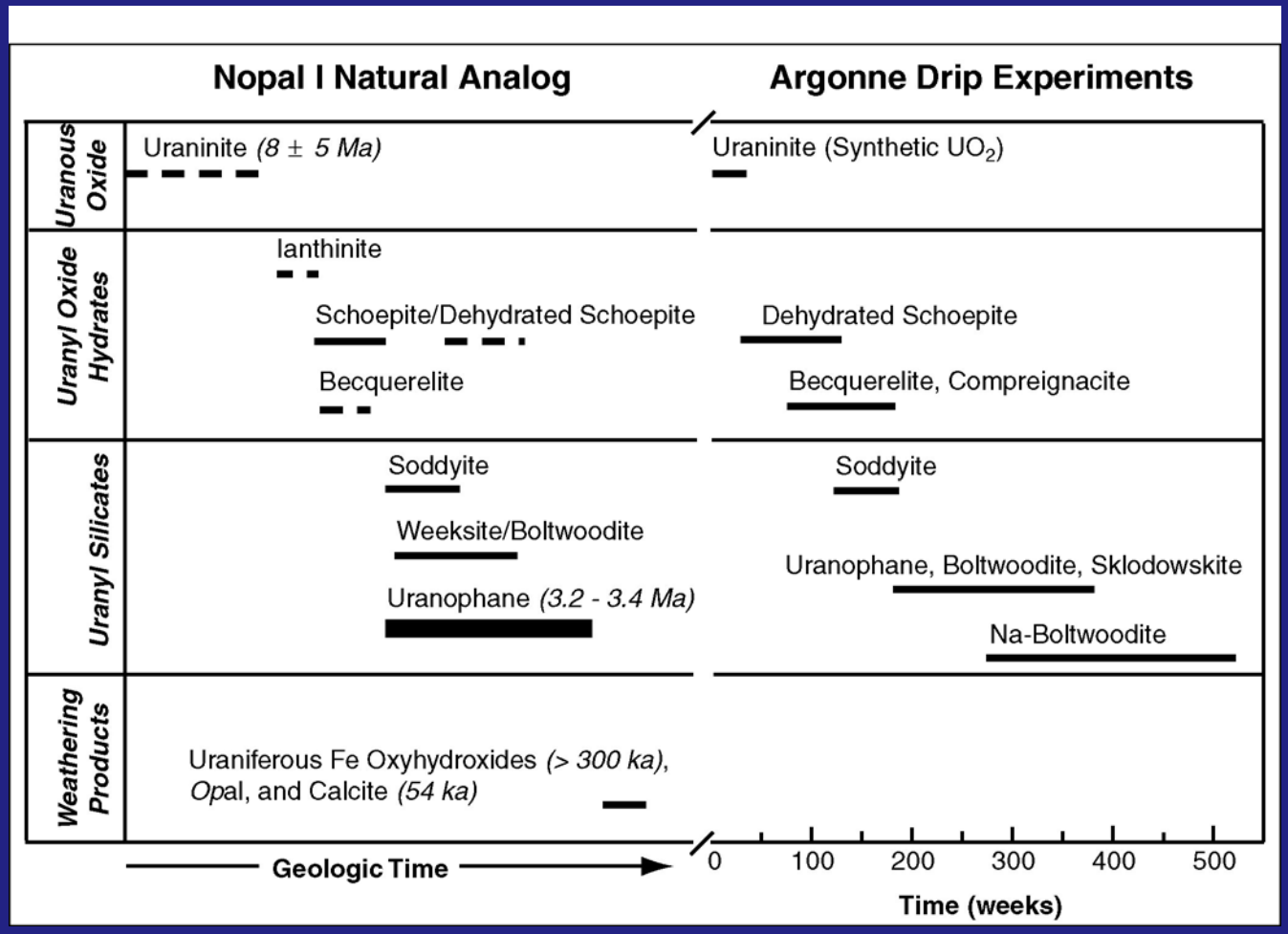
Analogous Paragenesis (Murphy, 2000)



Commentary on Uranium Mineralization at Nopal I

Given the epithermal character of the deposits and the lack of any identifiable intrusive rocks, the source of the uranium probably was not magmatic-hydrothermal. The uranium more likely was derived from the alteration and leaching of volcanic glass by geothermal convective groundwater systems.… Mineral deposition was accompanied by rock alteration and possibly was instigated by the presence of reducing waters derived from the organic- and pyrite?-rich basin sediments.… Apparently the deposit has been secondarily oxidized, because rare remnants of primary uraninite occur in the breccia. (Goodell, 1981)

Commentary on Uranium Mineralization at Nopal I (Continued)

Mixing of waters from both sources could occur in a fractured high permeability zone. The reducing water contained Fe^{2+} and HS^- derived from the carbonates, and the oxidizing water contained UO_2^{2+} derived from the tuff. Reaction of these fluids with feldspar of the tuff can be generalized by

$$UO_2^{2+} + Fe^{2+} + 2\ HS^- + H_2O + 2\ KAlSi_3O_8$$

$$\rightarrow UO_2 + FeS_2 + Al_2Si_2O_5(OH)_4 + 4\ SiO_2 + 2\ K^+$$

(Murphy, Pearcy, and Pickett, 1997)

Commentary on Uranium Mineralization at Nopal I (Continued)

High porosity pyroclastic tuffs were mineralized by deposits of secondary [uranyl] silicates resulting from leaching of overlying pitchblende by meteoritic water. (Calas, 1977)

Several remobilization stages, either hydrothermal or supergene, occur after the pitchblende-pyrite stage and lead to current oxidized mineralizations. … Fluid inclusions from opals associated with uranophane needles give a temperature of 150 ºC [300 ºF]. (George-Aniel, Leroy, and Poty, 1985)

Ultimate secondary mineral parageneses are made of halloysite and smectitie, β-uranophane and opal. …These secondary alteration minerals may be related to low-temperature alteration {< 100 ºC [212 ºF]}. (Ildefonse, Muller, Clozel, and Calas, 1990)

Dissolution Reactions

$UO_3 \cdot 2H_2O + 2\ H^+ \Leftrightarrow UO_2^{2+} + 3\ H_2O$
Metaschoepite

$(UO_2)_2SiO_4 \cdot 2H_2O + 4\ H^+$
Soddyite $\Leftrightarrow 2\ UO_2^{2+} + Si(OH)_4 + 2\ H_2O$

$Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O + 6\ H^+ \Leftrightarrow$
Uranophane $Ca^{2+} + 2\ UO_2^{2+} + 2\ Si(OH)_4 + 5\ H_2O$

Thermodynamic Data at 25 ºC [77 ºF]

Dissolution Reaction	Log K 25 ºC (77 ºF)	ΔH^o_r kJ/mol (kcal/mol)	Sources (Log K; ΔH^o_r)
Metaschoepite	4.81	-50.39 (-12.04)	NEA, 2003
Soddyite	5.35	-88.29 (-21.10)	*GH; this work
Uranophane	10.93	-130.23 (-31.13)	*P; this work

*GH: Giammar and Hering (2002) interpretation of Nguyen, et al. (1992) soddyite solubility

*P: Prikryl, et al. (2005) reversed uranophane solubility

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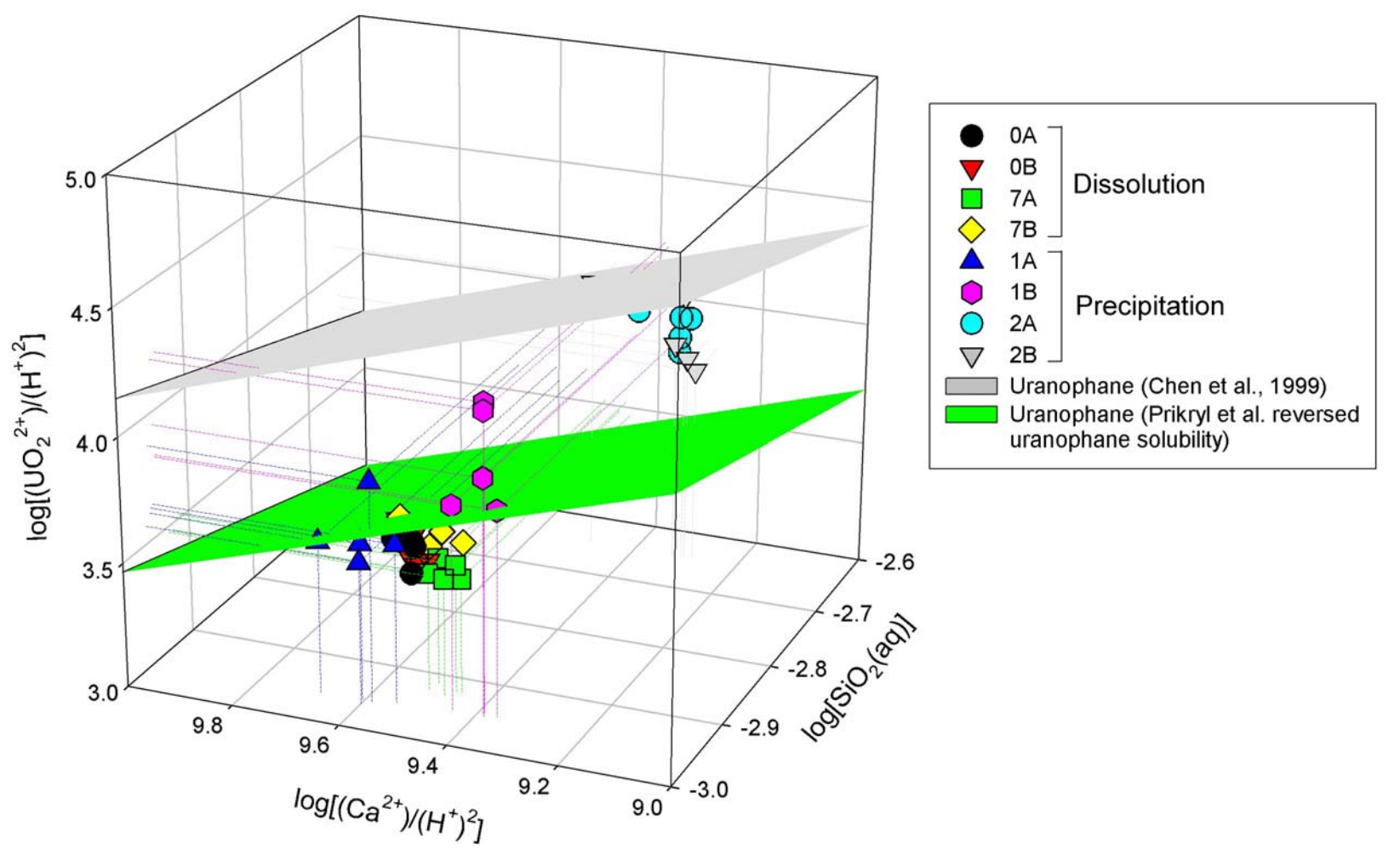
Reversed Uranophane Solubility Measurements at 25 ºC [77 ºF]



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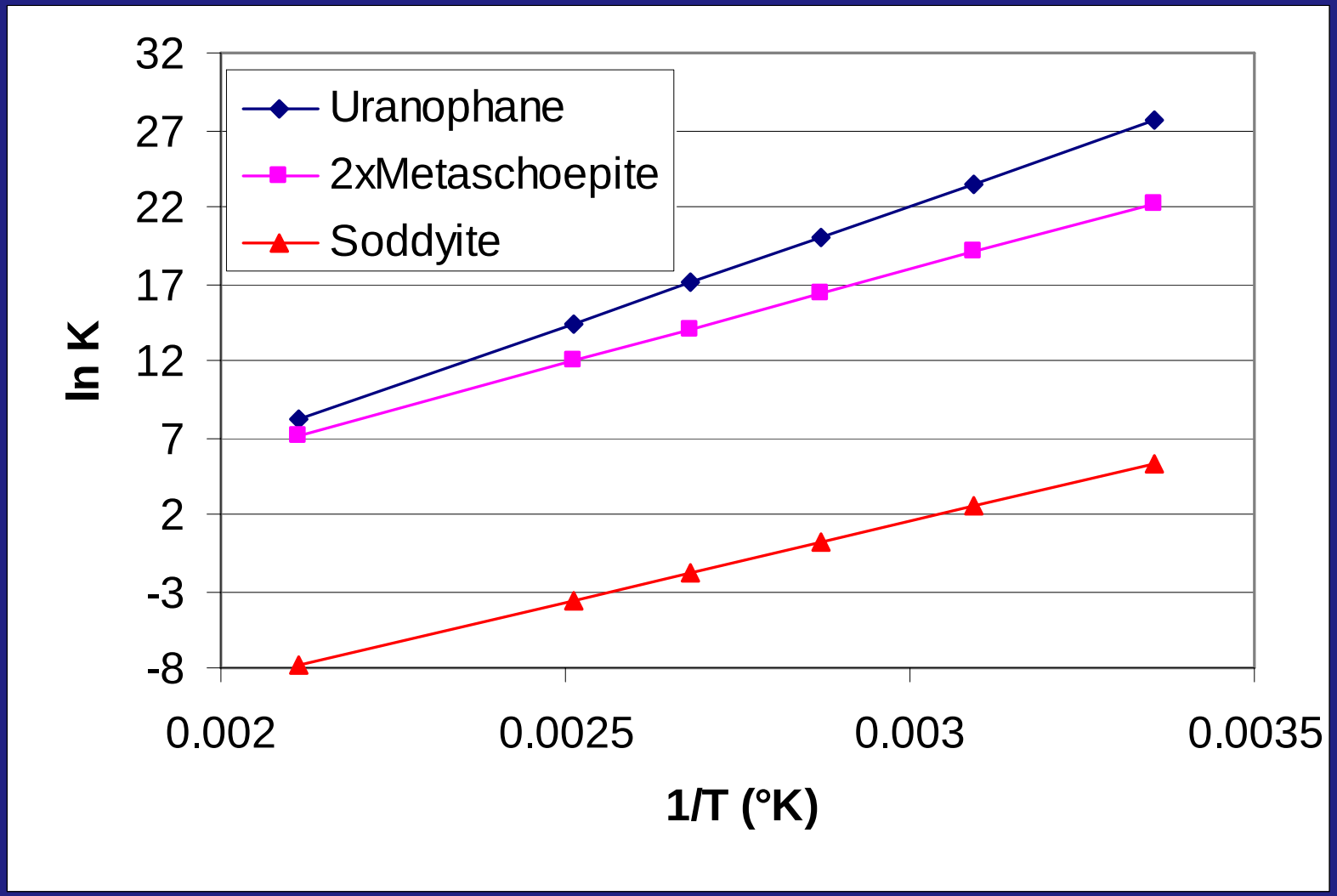
Retrograde Solubilities of Uranyl Minerals



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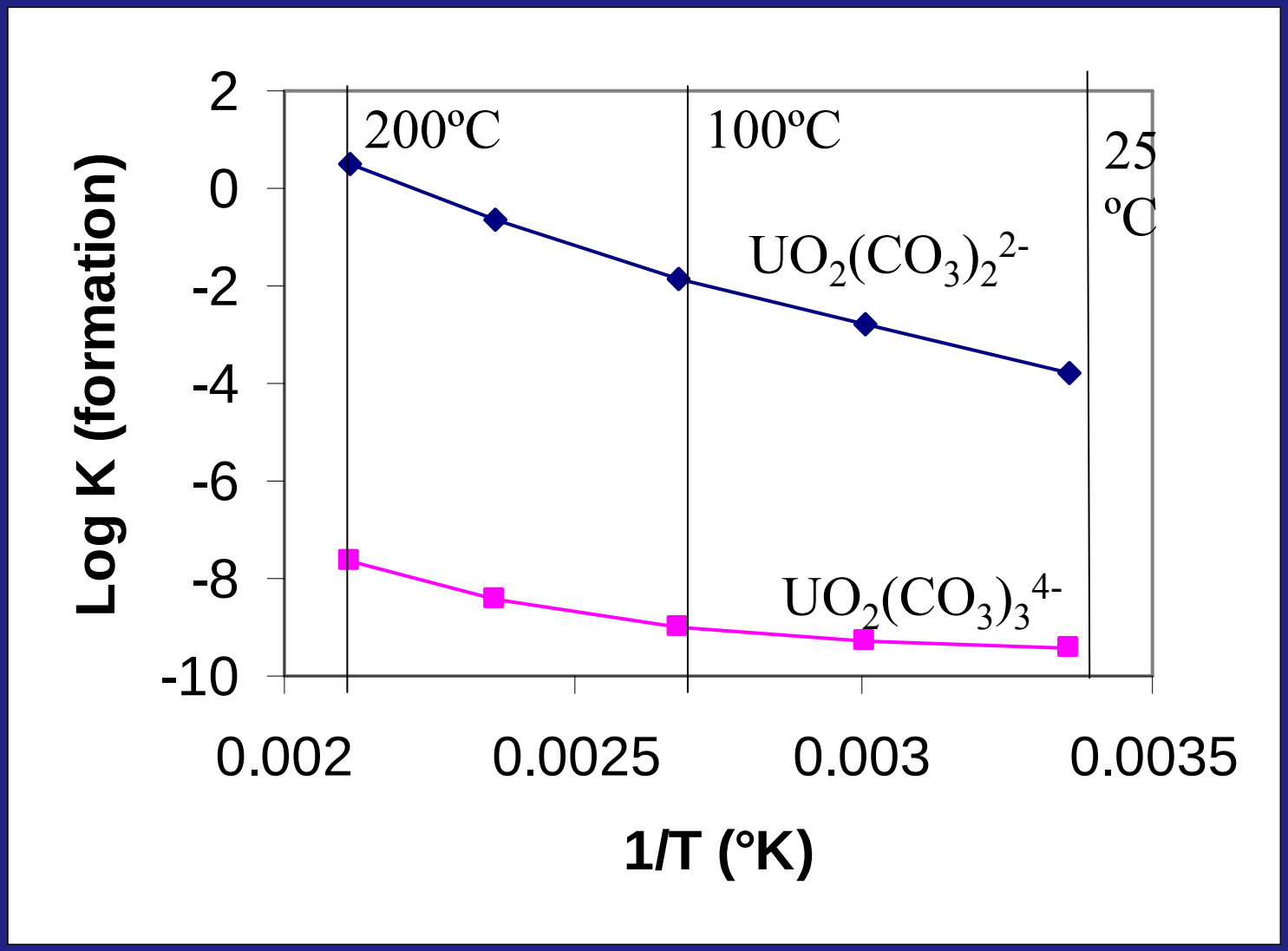
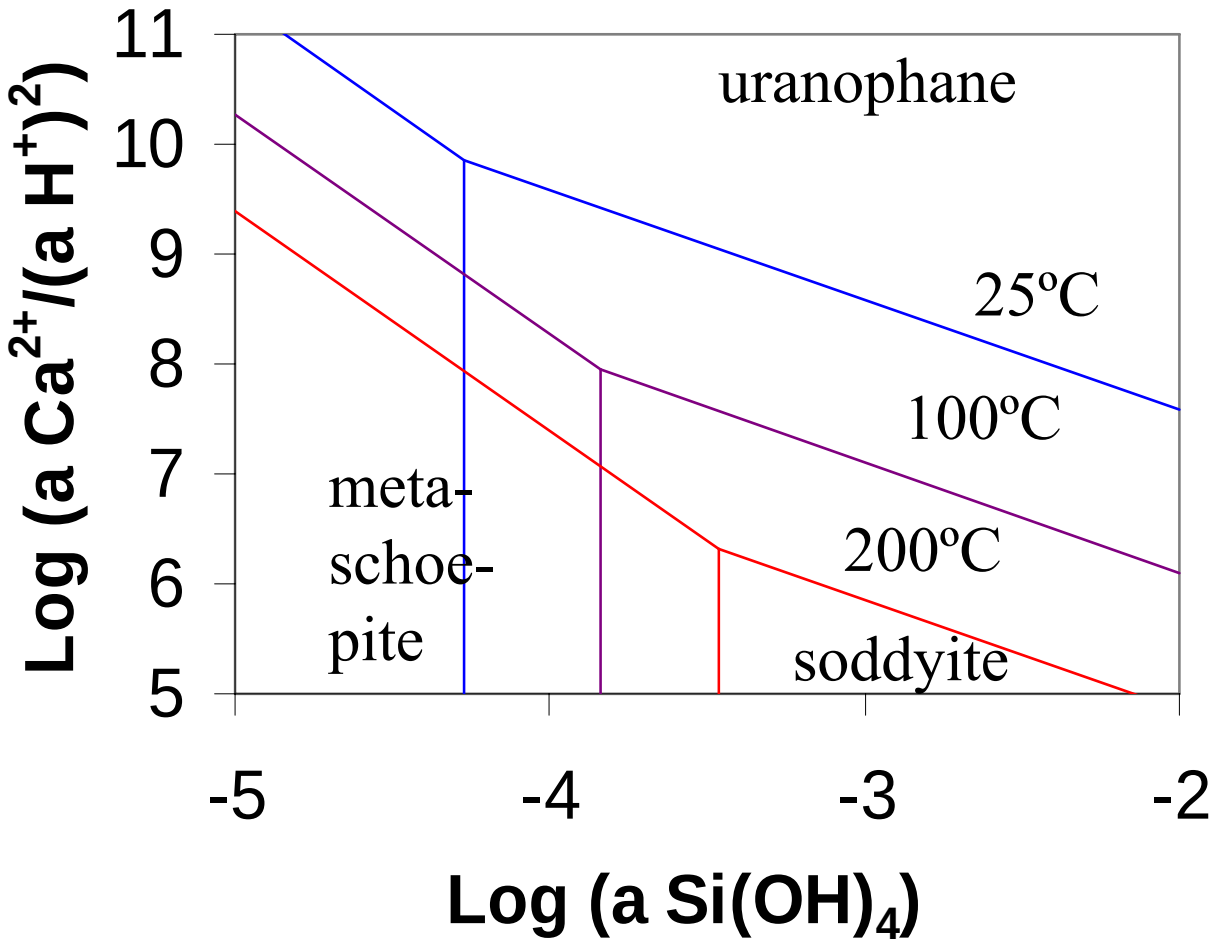
Stability of Uranyl Carbonate Complexes



Uranyl Mineral Stability



Log
(a UO_2^{2+}/
(a H^+)^2)
(metaschoepite equilibrium)

4.81 at 25 ºC
[77 ºF]
3.04 at 100 ºC
[212 ºF]
1.55 at 200 ºC
[392 ºF]

Observations on Phase Relations

Maximum aqueous uranyl concentrations, reflected by metaschoepite solubility, drop with increasing temperature, but the increasing stability of uranyl carbonate complexes with increasing temperature can lead to increasing uranium concentrations.

Metaschoepite - soddyite equilibrium buffers aqueous silica at values below quartz solubility at all temperatures.

Observations on Phase Relations

Uranophane stability increases dramatically with increasing temperature relative to metaschoepite and soddyite.

(The temperature dependence of uranyl carbonate complexes does not affect the relative stabilities of the uranyl minerals as a function of temperature.)

Concluding Remarks

Uranyl mineral occurrences at Nopal I are similar to those in experiments at 95 ºC [203 ºF] designed to mimic the potential repository at Yucca Mountain.

The paragenetic sequence:

metaschoepite - soddyite - uranophane

may represent open-system chemical evolution and progressive incorporation of environmental components in uranyl minerals.

Concluding Remarks (Continued)

At Nopal I this uranyl mineral sequence may be affected by prograde hydrothermal alteration and the relative retrograde temperature dependence of uranyl mineral stabilities.

Secondary mineral formation at Nopal I under weathering conditions is dominated by uraniferous calcite and amorphous silica.

Acknowledgment

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