

***Interpretation of
Hydrogeochemical
Evolution and ^{14}C Ages***

Ruprechtov 2003

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1 Introduction

The Ruprechtov site is located in the Sokolov basin in the North-West of Bohemia in Czech Republic. The Tertiary sediments of Oligocene and Miocene age are underlined by Carboniferous granitic rocks. There are significant concentrations of uranium in both ground water and in kaolinite formation. This site is considered as a potential analog of radionuclides migration from nuclear waste repository (UJV, 2001, 2002).

There was drilling of new wells in Summer 2002. New geochemical data were acquired and they are interpreted in the partial report released in Fall 2002. There was sampling for chemical and isotopic analysis in January 2003. The objective of this report is to present improved conceptual model of geochemical evolution and uranium migration at Ruprechtov site. The emphasis is placed on determination of radiocarbon ages and on better understanding of carbon cycling between several reservoirs.

This text is continuation of partial report from December 2003. Recently more data became available, thus making possible to test several conceptual models. Sampling for isotopic analysis has been performed in February 2003 and results of $^{14}\text{C}(\text{DIC})$ and $^{13}\text{C}(\text{DIC})$ determination became available in March 2003. These results are discussed in this partial report. Emphasis is placed on carbon cycling between several pools including dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), soil organic carbon (SOC), carbon in methane (C_{CH_4}), and also carbon in endogenous CO_2 ($\text{C}_{\text{CO}_2\text{-endog}}$). So far, there was a strong discrepancy between low hydraulic ages calculated on the basis of assumption of recharge area close to Ruprechtov village and isotopic ages, suggesting very old ground water. The aim of this text is to explain the discrepancy. Data used for interpretation were taken along presumed flow path between wells NA-8, NA-9, and NA-4.

2 Ground water chemistry evolution

Ground water was sampled in shallow domestic well in village Ruprechtov. Data from well NA-8 in recharge zone, well NA-9 at mid-distance between recharge zone and existing wells NA-4 and NA-5 in downgradient zone are presented in Table 1.

General observations:

- The pH values generally increase downgradient. This is consistent with consumption of CO_2 in kaolinization of feldspars in reaction like
$$\text{Feldspar} + \text{CO}_2 + \text{H}_2\text{O} = \text{kaolinite} + \text{alkaline ions} + \text{bicarbonate}$$

Parameter/Well	NA-8	NA-9	NA-5	NA-4
T[°C]	6.7	(7.2)	8.7	9.4
pH	7.0	(6.8)	7.4	6.9
EC [mS.m ⁻¹]	181		605	497
Eh[mV]	190	(171)	-138	-77
O ₂ [mg/L]	3.7	5.1	-	-
CH ₄ [mg/L]	-	-	-	1.2
Na	10	12	36	23
Ca	23	29	55	44
Mg	4.8	4.44	21	19
K	1.6	4.9	15	13
Alkalinity[mmol/L-mg/L HCO ₃]	0.68 (41)	2.46 (150)	6.5 (396.5)	5.05 (308.1)
SO ₄	50	13	21.7	24.6
Cl	4.3	1.8	3.37	2.21
F	0.33	1.0	0.6	1.21
PO ₄	0.28	<0.04	-	-
Al	0.01(0.26)	0.014 (0.13)	0.0082 (0.0672)	0.0363 (0.0786)
Ba	0.04	0.09	0.13	0.11
Fe	0.08(1.4)	0.18 (0.41)	0.81 (1.18)	1.86 (2.16)
Mn	0.57	1.31	0.25 (0.27)	0.075
U	0.0011 (0.0023)	0.0011	0.00063 (0.00083)	0.00009 (0.00017)
Si	15	17	10	14
NO ₃	<2.0	<2.0	0.08	<0.07
NH ₄	0.08	<0.05	1.02	1.22

Note: n.a.- not available

Table 1: Water chemistry in wells at Ruprechtov site. Concentrations are in mg/L

- Value of alkalinity generally increases downgradient, probably as a consequence of redox reactions such as oxidation of organic matter, in reactions like



and other redox reactions like denitrification and sulfate reduction. However, the downgradient change of alkalinity is very significant and an input of endogenic CO₂ cannot be ruled out (see later).

- Value of electrical conductivity (EC) increases downgradient as a consequence of increasing concentrations of redox reaction products and incongruent dissolution of feldspars.
- Concentration of Cl decreases downgradient and this behavior makes questionable the assumption about hydraulic connection between sampling points. There is a

possibility, however, that at least a part of downgradient water comes from mixing with water that did not recharge at village Ruprechtov.

3 Redox trends

- The Eh values trend indicates evolution from oxic and suboxic towards strongly reducing conditions. Nitrate and sulfate concentrations generally decrease downgradient, suggesting nitrate and sulfate reduction. However, sulfate concentrations at wells NA-4 and NA-5 increase again in comparison to well NA-9, and this behaviour makes questionable hydraulic connection between wells (see later).
- Redox conditions seem to be still out of methanogenesis region, except for well NA-4. Concentrations of dissolved methane increase from non-detectable levels in recharge zone towards value about 1.2 mg/L in well NA-4. This evolution is consistent with other redox parameters and with decreasing Eh values. Gradual decrease of Eh values from recharge zone downgradient probably corresponds to reaction of electron acceptors with organic matter, presumably in solid phase.

4 Organic carbon in ground water

There was sampling for total organic carbon (TOC) and dissolved organic carbon (DOC) determination. The distinction between both samples is in filtering of DOC sample through a filter 0.45 μm . Thus, if there is no organic carbon in colloidal form, the concentration of DOC = TOC. Results are in Table 2.

Results are surprising because in some cases DOC > TOC, for example, in samples from wells NA-8 and NA-9. In well NA-8, the difference is by more than 50 %. In other wells, the concentrations of DOC are lower than concentrations of TOC. Concentrations of organic carbon are significant and organic carbon may play a significant role in both complexation and facilitated transport of uranium and other species.

Also, it seems that frequently TOC \approx DOC, and this behavior indicates that colloidal facilitated transport in the form of organic colloids is probably as significant as complexation.

Well/Para-meter	NA-4	NA-5	NA-8	NA-9
TOC [mg/L]	4.6	6.5	5.8	6.2
DOC [mg/L]	3.7	5.7	9.2	6.3

Table 2: TOC and DOC

5 Speciation calculations

Program PHREEQC-2 (Parkhurst and Appelo 1999) was used for speciation calculations. Database for radionuclides was extended using database lnl (Lawrence Livermore National Laboratories) and the database of program MINTEQA2 (Allison et al., 1991) was also used. Results of calculations are in Table 3. Total concentrations of U were divided on the basis of field values of Eh. Only samples NA-8 and NA-4 were used for calculation. Sample NA-9 has similar water composition as sample NA-8, but redox potential measurement is missing and, thus, uranium in this sample cannot be speciated.

Speciation calculation indicated that in well NA-8 most of total dissolved U is present as U(VI). Phosphate complex $\text{UO}_2(\text{HPO}_4)_2^{2-}$ and carbonate complexes like $\text{UO}_2(\text{CO}_2)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_0^0$ predominate. Concentration of U(IV) is $\ll 1.0\%$ of total U and its principal form is $\text{U}(\text{OH})_5^-$. U(IV) becomes much more important in well NA-4. Here concentration of U(IV) reaches 3.02×10^{-10} mol/L and dominant form of U(IV) is $\text{U}(\text{OH})_5^-$ again. However, concentration of U(VI) is still significant, reaching 6.96×10^{-11} mol/L. The most important form of U(VI) are carbonate complexes $\text{UO}_2(\text{CO}_2)_2^{2-}$ and $\text{UO}_2(\text{CO}_2)_3^{4-}$ with concentrations 5.09×10^{-11} mol/L, and 1.38×10^{-11} mol/L, respectively.

Saturation indices for U minerals are negative, except for well NA-4 with positive values for uraninite. This is a consequence of a significant concentration of dissolved U(IV) under strongly reducing conditions. However, application of Eh values in speciation of U makes calculated SI values for uranium minerals questionable and caution has to be applied in their interpretation. Saturation for calcite and dolomite is not reached even in sample NA-4 with high value of alkalinity. Sample NA-4 has positive $\text{SI}_{\text{siderite}}$ and, thus, precipitation of this mineral phase may control concentration of dissolved iron.

Mineral/Well	NA-8	NA-4
Uraninite	-8.28	0.54
UO ₂ (am)	-10.98	-2.30
Calcite	-1.66	-0.65
Dolomite	-3.93	-1.56
Kaolinite	5.60	4.75
Al(OH) ₃ (am)	-1.10	-1.44
Goethite	5.83	2.23
Gypsum	-2.63	-2.82
Barite	-0.22	-0.29
Siderite	-1.93	0.09
Manganite	-6.17	-12.09
Ningyoite	-11.59	n.a.
SiO ₂ (a)	-0.73	-0.78
U(IV)(mol/L)	4.93x10 ⁻¹⁹	3.02x10 ⁻¹⁰
U(VI)(mol/L)	4.62x10 ⁻⁹	6.96x10 ⁻¹¹
LogP _{CO₂} (atm)	-2.50	-1.51
DIC(mol/L)	8.58x10 ⁻⁴	6.73x10 ⁻³

n.a.-not available

Table 3: Selected speciation results

The most important findings are increasing DIC and P_{CO₂} values downgradient. This suggests an input of carbon. This cannot be explained by dissolution of carbonates because in that case P_{CO₂} would have decreased a SI values for carbonates like calcite would have been close to zero. Thus, an alternative source of carbon has to be sought (see later).

6 Isotopic applications

6.1 Background

Last sampling was focused on carbon isotopes. Quantification of all carbon sources has been recognized as an essential tool for ¹⁴C dating. Most of isotopic studies have been focused on DIC in ground water, which generally is the largest carbon pool in ground water. However, carbon in the form of dissolved organic carbon (DOC) and methane may also play an important role in carbon cycling (Aravena et al. 1995, Zeh et al. 1997). Origin of methane (biogenic vs. thermocatalytic) can be evaluated using ¹³C(CH₄) values. Very depleted values (less than -50 ‰) indicate biogenic origin of methane and, on the other hand, enriched values may indicate thermocatalytic origin of methane (Aravena et al. 1995).

There are several approaches, which can be used for ¹⁴C dating of DIC. They generally are based on adjustments of initial ¹⁴C activities for the influence of processes like exchange of carbon with CO₂ soil zone, dissolution of carbonates, and isotopic

exchange with carbonate minerals. Presence of reactions involving organic matter such as redox reactions and especially methanogenesis can greatly complicate situation. The geochemical program which can handle both inorganic and organic sources of carbon is NETPATH (Plummer et al. 1994). Thus, results of ^{13}C and ^{14}C determination can be implemented in inverse geochemical modeling. Finally, isotopic values for endogenous CO_2 can be taken from literature (e.g., Weinlich et al. 1998) because DIC at Ruprechtov sites contains a mixture of carbon from several sources.

6.2 Isotopic data

Results of sampling for carbon isotopes are in Table 4.

Well/parameter	^{14}C (PMC)	Uncorrected age (years)	^{13}C (DIC) (per mil.)	^{13}C (DOC) (per mil.)
NA-8	71.95	1361	-21.95	n.a.
NA-9	71.11	1378	-20.52	n.a.
NA-4	3.19	27158	-11.66	-26.9
NA-5	6.39	21412	-11.22	n.a.

Table 4: Isotopic data

The data are in sharp discrepancy between isotopic data and hydrogeochemical data. Instead of relatively smooth hydrogeochemical evolution suggested by hydrogeochemical data, there is a divide in isotopic data between wells NA-9 and NA-4. Values of ^{13}C (DIC) in ground water from wells are around -21 per mil. These results suggest source of carbon in organic matter and also in atmospheric CO_2 . The value of ^{13}C in soil organic matter ^{13}C (SOM) is not known, but it can be estimated as about -27 per mil. (Clark and Fritz, 1997). This also corresponds to value of ^{13}C (DOC) in ground water from well NA-4. Thus, soil organic matter is probably a source of TOC and DOC. On the other hand, these values are contradicting a possibility of a significant input of carbon from carbonates in solid phase. The ground water ages based on sampling from wells NA-8 and NA-9 are relatively low, about 1370 years. However, even these samples are probably influenced by the input of CO_2 generated in redox reactions, and, thus, their ages are probably overestimated.

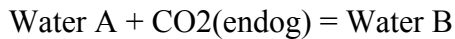
On the other hand, samples NA-4 and NA-5 have values of ^{13}C (DIC) much more enriched and reach about -11.5 per mil. Activities of ^{14}C are much lower and ground water ages are correspondingly higher, reaching 27000 years. Several possible scenarios can explain this evolution:

- (a) Wells NA-9 and NA-4 are not hydraulically connected. Thus, determination of ground water residence time between these samples does not make any sense.
- (b) There is an input of carbon from solid phase. Processes like dissolution of calcite,



would increase $^{13}\text{C}(\text{DIC})$ values in close system up to -11 per mil. and also apparent ground water ages based on $^{14}\text{C}(\text{DIC})$.

- (c) There is an input of endogenic CO_2 from deeper zone,



This process would result in increasing values of $^{13}\text{C}(\text{DIC})$ because ^{13}C value for endogenic CO_2 is about -3.0 per mil. (Weinlich et al., 1998). Also, the process would increase apparent ground water ages based on $^{14}\text{C}(\text{DIC})$ because endogenic CO_2 has 0 PMC activity of ^{14}C .

- (d) There is methanogenesis described like



The process results in production of isotopically depleted methane and isotopically enriched $^{13}\text{C}(\text{DIC})$ because light ^{12}C goes preferentially to methane and heavy ^{13}C goes to CO_2 . The impact on $^{14}\text{C}(\text{DIC})$ depends on the age of CH_2O . Assuming that CH_2O is soil organic matter of Tertiary age, then its ^{14}C is equal to 0 PMC. This means that the process results in low activity of $^{14}\text{C}(\text{DIC})$.

It is worth to mention that processes (b), (c), and (d) increase concentration of dissolved inorganic carbon (DIC) downgradient. On the other hand, in some cases increasing value of alkalinity can be related to increasing pH values in processes like dissolution of silicates and they do not necessarily prove carbon input.

- (e) There also is a possibility of combination of processes (b), (c), and (d) in different proportions.

7 Inverse geochemical modelling

7.1 Background

This type of modeling is used in cases, when we want to determine which reactions have already taken place between sampling points. There are two types of the mass balance modeling: interpretation of ground water chemistry between 2 sampling points and a mixing problem. In the case of chemical evolution, the input includes ground water chemistry of 2 hydraulically connected samples and composition of solid phase in the aquifer between these 2 points. In the case of mixing problem, the required input are at least 3 samples, which represent chemistry of 2 waters prior to mixing and chemistry of final water after mixing and after completion of geochemical reactions. Typical models of the type are NETPATH (Plummer et al., 1994) and PHREEQC-2 (Parkhurst and Appelo, 1999). The principal difference between both programs is the possibility to

include analytical uncertainty in Phreeqc-2. Programs are based on mass balance equation:

$$\Delta m_{T,K} = \sum \alpha_p b_{p,k} \quad k = 1,j$$

where $\Delta m_{T,K}$ is change of total dissolved concentration of k^{th} component between sampling points, α_p is the quantity of component p (for example, in mol/kg of water) which dissolved or precipitated and $b_{p,k}$ is stoichiometric coefficient of k^{th} component in p^{th} mineral. For example, for dissolved inorganic carbon change along flowpath with reacting phases including calcite, dolomite and $\text{CO}_2(\text{g})$, we can write

$$\Delta m_{T,C} = \alpha_{\text{calcite}} + 2\alpha_{\text{dolomite}} + \alpha_{\text{CO}_2}$$

Then the program solves a set of equations for specified components and the goal is to calculate mass transfer coefficient α for each phase. Similar equations are solved for balance of electrons and isotopes.

The output has the following form:

Water A + Reactants = Water B + Products

or, in the case of mixing

Water A + Water B + Reactants = Water C + Products

There are several problems of inverse geochemical modeling: (1) The water analysis from initial and final wells should represent packets of water that flow along the same flow path, (2) dispersion and diffusion do not significantly affect solution chemistry, (3) a chemical steady prevailed during the period considered, and (4) inter-aquifer mixing is insignificant. However, as we will discuss later in the text, especially assumption (1) is questionable at Ruprechtov site. Assumption (3) means constant water chemistry pattern in time and this is probably valid, except for recharge zone with recent anthropogenic contamination.

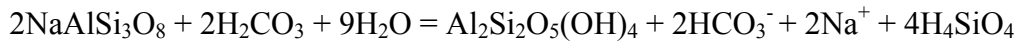
7.2 Inverse modelling

7.2.1 Conceptual geochemical model

Conceptual model is based on concentration data in Table 1 and on SI values in Table 3. Two profiles are considered: Profile 1 between wells NA-8/NA-9, and Profile 2 between wells NA-9/NA-4.

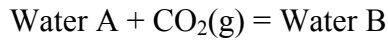
(a) dissolution of carbonates like calcite and/or dolomite.

- (b) dissolution of plagioclase and formation of kaolinite (process indicated by mineralogical evidence),



This process is considered on both Profile 1 and Profile 2.

- (c) an input of endogenic CO₂ via tectonics (Weinlich et al., 1998)



This process is considered only on Profile 2 because depleted values of ¹³C(DIC) on Profile 1 thus not support the hypothesis about isotopically heavy CO₂ input.

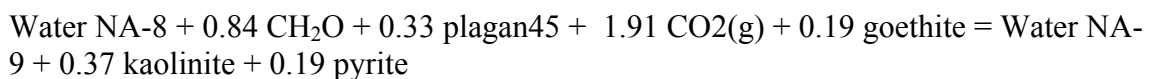
- (d) Various redox processes like oxidation of organic matter, reduction of nitrate, Fe(OH)₃, and sulfate, and precipitation of pyrite. These processes are considered on both profiles, but they probably play a minor role.
- (e) Methanogenesis discussed above, which is considered only on Profile 2 because there was no methane in all wells but well NA-4.

7.2.2 Results of inverse geochemical modeling

Two profiles have been modelled: Profile 1 included wells NA-8 and NA-9 close to assumed recharge zone downhill from Ruprechtov village and Profile 2, which included profile between well NA-9 and well NA-4.

In Model 1, selected constraints were: Ca, C, S, Fe, Si, and Redox. The constraint Redox accounts for conservation of electrons in redox reactions like oxidation of organic matter. Selected phases were: CH₂O, calcite, CO₂(g), plagan45 (plagioclase with 45% of anorthite component), kaolinite, goethite, and Ca/Na exchange. The phase rule stating that number of phases ≥ number of constraints is respected. None of phases indicated above has to be included in all models. Isotopic data for CO₂(g) used in modeling were: ¹³C in CO₂(g) equal to -25.0 per mil. and ¹⁴C(CO₂) equal to 100 PMC. The purpose for using of CO₂(g) with recent ¹⁴C activity was to account for a minimum difference in ¹⁴C activities between wells NA-8 and NA-4.

Possible reaction is:

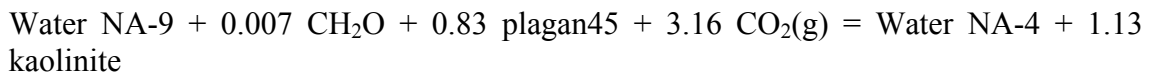


where numbers before mineral phases are transfer coefficients in mmol/L. The model accounts for increasing alkalinity and redox trends along flow path and is also consistent with observed formation of kaolinite. Dissolution of goethite is accepted in

spite of positive SI_{goethite} values because speciation of iron strongly depends on uncertain Eh values.

In Model 2, selected constraints were Ca, C, Si, Fe, and redox, selected phases were CH_2O , calcite, $\text{CO}_2(\text{g})$, plagan45, kaolinite, goethite, and Ca/Na exchange. In that case, values of $^{13}\text{C}(\text{CO}_2)$ equal to -3.0 per mil. and $^{14}\text{C}(\text{CO}_2)$ equal to 100 PMC were used, in agreement with hypothesis about endogenic $\text{CO}_2(\text{g})$ input and on the basis of results of previous investigations (for example, Weinlich et al. 1998).

Possible model is



This model is consistent with assumed input of endogenic $\text{CO}_2(\text{g})$. Results of ^{13}C mass balance and calculated travel times between wells based on ^{14}C are in Table 5.

Well/parameter	$\delta^{13}\text{C}$ calculated (per mil.)	$\delta^{13}\text{C}$ observed (per mil.)	Travel time (years)
NA-9	-24.7	-20.52	0*
NA-4	-12.31	-11.66	20416

* - in the range of error

Table 5: ^{13}C mass balance and ^{14}C travel times.

Results of carbon mass balance based on inverse modeling contradict the hypothesis about hydraulic connection between sampled wells. Relatively shallow wells NA-8 and NA-9 seems to be recharged in their proximity and there is zero travel time corresponding to flow between them. Also, it seems that DIC between these wells is generated in redox reactions with relatively recent organic matter. On the other hand, there is excessively long travel time (> 20000 years) between wells NA-9 and NA-4 calculated on the basis of carbon mass balance and $^{14}\text{C}(\text{DIC})$ data. The distance between wells NA-9 and NA-4 is 149 m, and taking the travel time indicated above, the average linear velocity of about $7.3 \times 10^{-3} \text{ m}\cdot\text{year}^{-1}$ is obtained. This value is lower than a travel distance for purely diffusive transport. Thus, it seems that ground water at well NA-4 represents a different flow system or, alternatively, corresponds to a relatively permeable zone of limited size.

Uranium is not included in NETPATH database, but precipitation of uraninite should follow the trend of increasingly reducing conditions along flow path. In that case, an electron donor like organic matter or Fe(II) is necessary, but regarding very low dissolved U_{total} concentrations in the order of 10^{-6} mol/L , the amount of reducing agent is relatively small and does not play a significant role in global mass balance.

8 Summary

- There is a trend of redox evolution from oxic to suboxic conditions in recharge area towards strongly reducing conditions in deep downgradient zone. There probably is relatively fast denitrification and no detectable nitrate is found in wells close to expected recharge area. Conditions become more reducing downgradient, with decreasing concentration of SO_4 and with relatively high concentration of dissolved methane in NA-4.
- This redox evolution has strong impact on dissolved U behaviour. In recharge zone, U is present as U(VI) and its solubility is enhanced by formation of carbonate complexes and also a complex with phosphate. Further downgradient, there is reduction of U(VI) with resulting formation of U(IV), which is present mostly as $\text{U}(\text{OH})_5^-$. Solubility product of uraninite is reached and these mineral phase precipitate. However, there probably also is adsorption of U on adsorbents in solid phase like organic matter. Precipitation of ningyoite, which was found in solid phase is not consistent with speciation calculations. However, this can be explained by precipitation of solid phase solution with ningyoite and rhabdophanes as end members.
- Isotopic analysis of carbon indicate a sharp change of isotopic behaviour between wells NA-9 and NA-4. Values of $^{13}\text{C}(\text{DIC})$ in wells NA-8 and NA-9 indicate input of DIC from redox reactions without a significant influence of carbonate dissolution. Ages based on $^{14}\text{C}(\text{DIC})$ are about 1350 years. On the other hand, value of $^{13}\text{C}(\text{DIC})$ for well NA-4 is much more enriched, reaching about - 11 per mil. This can be caused by various processes, including the input of endogenic CO_2 . Value of age based on $^{14}\text{C}(\text{DIC})$ is much higher, reaching more than 20000 years even when a potential input of dead carbon is taken into account.
- Hydraulic connection between sampling points on profile does not seem to be possible. Thus, conclusions above hydrogeochemical evolution are applicable as only general trends and they do not probably mean evolution along flow path. Potential future work could comprise installation and sampling of new well at mid-point between wells NA-9 and NA-4.

9 References

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Appendix A: Thermodynamic data used for uranium speciation

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SOLUTION_MASTER_SPECIES
  U      UO2+2  0.0  238.0290  238.0290
  U(4)   U+4    0.0  238.0290
  U(5)   UO2+   0.0  238.0290
  U(6)   UO2+2  0.0  238.0290
SOLUTION_SPECIES 1 # Do not change this number it is used by the program!
  UO2+2 = UO2+2
    log_k  0
    delta_h 0    kcal
  UO2+2 + e- = UO2+
    log_k  2.785
    delta_h -3.3  kcal
  UO2+2 + 2e- + 4H+ = U+4 + 2H2O
    log_k  9.216
    delta_h -34.43 kcal
  UO2+2 + 3e- + 4H+ = U+3 + 2H2O
    log_k  0.42
    delta_h -10.03 kcal
  U+4 + H2O = UOH+3 + H+
    log_k  -0.656
    delta_h 11.715 kcal
    analytical_expression -9.16  0.0285
  U+4 + 2H2O = U(OH)2+2 + 2H+
    log_k  -2.27
    delta_h 17.73  kcal
  U+4 + 3H2O = U(OH)3+ + 3H+
    log_k  -4.935
    delta_h 22.645 kcal
  U+4 + 4H2O = U(OH)4 + 4H+
    log_k  -8.498
    delta_h 24.76  kcal
  U+4 + 5H2O = U(OH)5- + 5H+
    log_k  -13.12
    delta_h 27.575 kcal
  6U+4 + 15H2O = U6(OH)15+9 + 15H+
    log_k  -17.229
    delta_h 0    kcal
  U+4 + F- = UF+3
    log_k  8.659
    delta_h 5.05  kcal
  U+4 + 2F- = UF2+2
    log_k  14.457
    delta_h 7.2   kcal
  U+4 + 3F- = UF3+
    log_k  19.115
    delta_h 7.15  kcal
  U+4 + 4F- = UF4
    log_k  23.64
    delta_h 4.6   kcal
  U+4 + 5F- = UF5-
    log_k  25.238
    delta_h 4.85  kcal
  U+4 + 6F- = UF6-2

```

\log_k 27.718
 ΔH 3.3 kcal
 $U^{+4} + Cl^- = UCl^{+3}$
 \log_k 1.338
 ΔH 9.933 kcal
 $U^{+4} + SO_4^{2-} = USO_4^{+2}$
 \log_k 5.461
 ΔH 3.7 kcal
 $U^{+4} + 2SO_4^{2-} = U(SO_4)_2$
 \log_k 9.749
 ΔH 7.6 kcal
 $U^{+4} + PO_4^{3-} + H^+ = UHPO_4^{+2}$
 \log_k 24.443
 ΔH 7.5 kcal
 $U^{+4} + 2PO_4^{3-} + 2H^+ = U(HPO_4)_2$
 \log_k 46.833
 ΔH 1.7 kcal
 $U^{+4} + 3PO_4^{3-} + 3H^+ = U(HPO_4)_3^{2-}$
 \log_k 67.564
 ΔH -7.8 kcal
 $U^{+4} + 4PO_4^{3-} + 4H^+ = U(HPO_4)_4^{4-}$
 \log_k 88.483
 ΔH -26.5 kcal
 $UO_2^{+2} + H_2O = UO_2OH^+ + H^+$
 \log_k -5.09
 ΔH 10.216 kcal
 $2UO_2^{+2} + 2H_2O = (UO_2)_2(OH)_2^{+2} + 2H^+$
 \log_k -5.645
 ΔH 10.23 kcal
 $3UO_2^{+2} + 5H_2O = (UO_2)_3(OH)_5^{+5} + 5H^+$
 \log_k -15.593
 ΔH 25.075 kcal
 $UO_2^{+2} + CO_3^{2-} = UO_2CO_3$
 \log_k 10.071
 ΔH 0.84 kcal
analytical_expression -9.56 0.03434 2809.0
 $UO_2^{+2} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$
 \log_k 17.008
 ΔH 3.48 kcal
analytical_expression 14.14 0.0096
 $UO_2^{+2} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$
 \log_k 21.384
 ΔH -8.78 kcal
 $UO_2^{+2} + F^- = UO_2F^+$
 \log_k 5.105
 ΔH -0.45 kcal
 $UO_2^{+2} + 2F^- = UO_2F_2$
 \log_k 8.92
 ΔH -0.9 kcal
 $UO_2^{+2} + 3F^- = UO_2F_3^-$
 \log_k 11.364
 ΔH -0.85 kcal
 $UO_2^{+2} + 4F^- = UO_2F_4^{2-}$
 \log_k 12.607
 ΔH -1.1 kcal
 $UO_2^{+2} + Cl^- = UO_2Cl^+$
 \log_k 0.22

$\text{delta_h } 1.233 \text{ kcal}$
 $\text{UO}_2+2 + \text{SO}_4-2 = \text{UO}_2\text{SO}_4$
 $\text{log_k } 2.709$
 $\text{delta_h } 5.1 \text{ kcal}$
 $\text{UO}_2+2 + 2\text{SO}_4-2 = \text{UO}_2(\text{SO}_4)_2-2$
 $\text{log_k } 4.183$
 $\text{delta_h } 6.1 \text{ kcal}$
 $\text{UO}_2+2 + \text{PO}_4-3 + \text{H}^+ = \text{UO}_2\text{HPO}_4$
 $\text{log_k } 20.814$
 $\text{delta_h } -2.1 \text{ kcal}$
 $\text{UO}_2+2 + 2\text{PO}_4-3 + 2\text{H}^+ = \text{UO}_2(\text{HPO}_4)_2-2$
 $\text{log_k } 42.988$
 $\text{delta_h } -11.399 \text{ kcal}$
 $\text{UO}_2+2 + \text{PO}_4-3 + 2\text{H}^+ = \text{UO}_2\text{H}_2\text{PO}_4+$
 $\text{log_k } 22.643$
 $\text{delta_h } -3.7 \text{ kcal}$
 $\text{UO}_2+2 + 2\text{PO}_4-3 + 4\text{H}^+ = \text{UO}_2(\text{H}_2\text{PO}_4)_2$
 $\text{log_k } 44.7$
 $\text{delta_h } -16.5 \text{ kcal}$
 $\text{UO}_2+2 + 3\text{PO}_4-3 + 6\text{H}^+ = \text{UO}_2(\text{H}_2\text{PO}_4)_3-$
 $\text{log_k } 66.245$
 $\text{delta_h } -28.6 \text{ kcal}$
 $\text{UO}_2+2 + \text{H}_4\text{SiO}_4 = \text{UO}_2\text{H}_3\text{SiO}_4+ + \text{H}^+$
 $\text{log_k } -2.4$
 $\text{delta_h } 0 \text{ kcal}$
 PHASES 1 # Do not change this number it is used by the program!
 Uraninite
 $\text{UO}_2 + 4\text{H}^+ = \text{U}+4 + 2\text{H}_2\text{O}$
 $\text{log_k } -4.7$
 $\text{delta_h } -18.63 \text{ kcal}$
 UO2(am)
 $\text{UO}_2 + 4\text{H}^+ = \text{U}+4 + 2\text{H}_2\text{O}$
 $\text{log_k } 0.934$
 $\text{delta_h } -26.23 \text{ kcal}$
 U4O9(C)
 $\text{U}_4\text{O}_9 + 18\text{H}^+ + 2\text{e}^- = 4\text{U}+4 + 9\text{H}_2\text{O}$
 $\text{log_k } -3.384$
 $\text{delta_h } -101.235 \text{ kcal}$
 U3O8(C)
 $\text{U}_3\text{O}_8 + 16\text{H}^+ + 4\text{e}^- = 3\text{U}+4 + 8\text{H}_2\text{O}$
 $\text{log_k } 21.107$
 $\text{delta_h } -116.02 \text{ kcal}$
 USiO4(C)
 $\text{USiO}_4 + 4\text{H}^+ = \text{U}+4 + \text{H}_4\text{SiO}_4$
 $\text{log_k } -7.62$
 $\text{delta_h } -14.548 \text{ kcal}$
 UF4(C)
 $\text{UF}_4 = \text{U}+4 + 4\text{F}^-$
 $\text{log_k } -18.606$
 $\text{delta_h } -18.9 \text{ kcal}$
 UF4:2.5H2O
 $\text{UF}_4:2.5\text{H}_2\text{O} = \text{U}+4 + 4\text{F}^- + 2.5\text{H}_2\text{O}$
 $\text{log_k } -27.57$
 $\text{delta_h } -0.588 \text{ kcal}$
 U(HPO4)2
 $\text{U}(\text{HPO}_4)_2 = \text{U}+4 + 2\text{PO}_4-3 + 2\text{H}^+$
 $\text{log_k } -51.584$

ΔH 3.84 kcal
 Ningyoite
 $\text{CaU}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O} = \text{U}^{4+} + \text{Ca}^{2+} + 2\text{PO}_4^{3-} + 2\text{H}_2\text{O}$
 $\log K$ -53.906
 ΔH -2.27 kcal
 UO₃(C)
 $\text{UO}_3 + 2\text{H}^+ = \text{UO}_2^{2+} + \text{H}_2\text{O}$
 $\log K$ 7.719
 ΔH -19.315 kcal
 Gummite
 $\text{UO}_3 + 2\text{H}^+ = \text{UO}_2^{2+} + \text{H}_2\text{O}$
 $\log K$ 10.403
 ΔH -23.015 kcal
 B_UO₂(OH)₂
 $\text{UO}_2(\text{OH})_2 + 2\text{H}^+ = \text{UO}_2^{2+} + 2\text{H}_2\text{O}$
 $\log K$ 5.544
 ΔH -13.73 kcal
 Schoepite
 $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O} + 2\text{H}^+ = \text{UO}_2^{2+} + 3\text{H}_2\text{O}$
 $\log K$ 5.404
 ΔH -12.045 kcal
 Rutherfordine
 $\text{UO}_2\text{CO}_3 = \text{UO}_2^{2+} + \text{CO}_3^{2-}$
 $\log K$ -14.439
 ΔH -1.44 kcal
 analytical_expression 4.54 -0.03318 -2716.0
 (UO₂)₃(PO₄)₂
 $(\text{UO}_2)_3(\text{PO}_4)_2 = 3\text{UO}_2^{2+} + 2\text{PO}_4^{3-}$
 $\log K$ -49.037
 ΔH 94.9 kcal
 H-Autunite
 $\text{H}_2(\text{UO}_2)_2(\text{PO}_4)_2 = 2\text{H}^+ + 2\text{UO}_2^{2+} + 2\text{PO}_4^{3-}$
 $\log K$ -47.931
 ΔH -3.6 kcal
 Na-Autunite
 $\text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2 = 2\text{Na}^+ + 2\text{UO}_2^{2+} + 2\text{PO}_4^{3-}$
 $\log K$ -47.409
 ΔH -0.46 kcal
 K-Autunite
 $\text{K}_2(\text{UO}_2)_2(\text{PO}_4)_2 = 2\text{K}^+ + 2\text{UO}_2^{2+} + 2\text{PO}_4^{3-}$
 $\log K$ -48.244
 ΔH 5.86 kcal
 Uramphite
 $(\text{NH}_4)_2(\text{UO}_2)_2(\text{PO}_4)_2 = 2\text{UO}_2^{2+} + 2\text{NH}_4^+ + 2\text{PO}_4^{3-}$
 $\log K$ -51.749
 ΔH 9.7 kcal
 Saleeite
 $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 = 2\text{UO}_2^{2+} + \text{Mg}^{2+} + 2\text{PO}_4^{3-}$
 $\log K$ -43.646
 ΔH -20.18 kcal
 Autunite
 $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 = 2\text{UO}_2^{2+} + \text{Ca}^{2+} + 2\text{PO}_4^{3-}$
 $\log K$ -43.927
 ΔH -14.34 kcal
 Sr-Autunite
 $\text{Sr}(\text{UO}_2)_2(\text{PO}_4)_2 = 2\text{UO}_2^{2+} + \text{Sr}^{2+} + 2\text{PO}_4^{3-}$
 $\log K$ -44.457

delta_h -13.05 kcal
 Uranocircite
 $\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 = 2\text{UO}_2+2 + \text{Ba}+2 + 2\text{PO}_4-3$
 log_k -44.631
 delta_h -10.1 kcal
 Bassetite
 $\text{Fe}(\text{UO}_2)_2(\text{PO}_4)_2 = 2\text{UO}_2+2 + \text{Fe}+2 + 2\text{PO}_4-3$
 log_k -44.485
 delta_h -19.9 kcal
 Torbernite
 $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 = 2\text{UO}_2+2 + \text{Cu}+2 + 2\text{PO}_4-3$
 log_k -45.279
 delta_h -15.9 kcal
 Przhevalskite
 $\text{Pb}(\text{UO}_2)_2(\text{PO}_4)_2 = 2\text{UO}_2+2 + \text{Pb}+2 + 2\text{PO}_4-3$
 log_k -44.365
 delta_h -11 kcal
 Uranophane
 $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 + 6\text{H}+ = 2\text{UO}_2+2 + \text{Ca}+2 + 2\text{H}_4\text{SiO}_4$
 log_k 17.49
 delta_h -0 kcal
 $\text{UO}_2(\text{NO}_3)_2$
 $\text{UO}_2(\text{NO}_3)_2 = \text{UO}_2+2 + 2\text{NO}_3-$
 log_k 12.369
 delta_h -20.14 kcal
 $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
 $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} = \text{UO}_2+2 + 2\text{NO}_3- + 2\text{H}_2\text{O}$
 log_k 4.851
 delta_h -6.06 kcal
 $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$
 $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} = \text{UO}_2+2 + 2\text{NO}_3- + 3\text{H}_2\text{O}$
 log_k 3.642
 delta_h -2.405 kcal
 $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
 $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = \text{UO}_2+2 + 2\text{NO}_3- + 6\text{H}_2\text{O}$
 log_k 2.3
 delta_h 4.77 kcal



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