

The Chemistry of Uranium Dispersion in Groundwaters at the Pinhal Do Souto Mine, Portugal

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Abstract

Solution studies of H-autunite, $\text{H}_2(\text{UO}_2)_2(\text{PO}_4)_2$, and its K^+ , Na^+ , Li^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} and Ni^{2+} analogues, have been carried out and solution stability constants determined. These values are in excellent agreement with those recently reported by other workers at 298.2 K and ionic strength equal to zero. A separate field study involving groundwaters collected from the oxidized zone of the Pinhal do Souto mine, Portugal, has been undertaken. Here the principal uranium minerals are autunite, $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ and torbernite $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$. Detailed analyses of and calculations of species distributions in these samples indicate that currently circulating groundwaters are undersaturated with respect to these two minerals by two to four orders of magnitude. The mineralogical and geochemical significance of these results is discussed.

Introduction

Considerable attention has been focused upon solution equilibria of actinide complexes containing simple inorganic ligands [1]. Much of this work, particularly in recent years, stems from an appreciation of the need to understand chemical processes involved with the nuclear fuel cycle. In addition, natural geochemical cycles involving the emplacement of uranium orebodies, their reactions and transformations upon oxidation by circulating groundwaters and the dispersion of uranium in their vicinity is of interest to many groups of workers. These include mineralogists and exploration geochemists. Accordingly, a great deal of effort has been directed towards the accumulation of thermodynamic data for secondary uranium minerals, particularly those containing the uranyl, UO_2^{2+} , ion [1–5].

One aim of these studies and ours in particular, [3], is to develop a thermodynamic model which can be used to explain some of the chemical conditions obtaining during the crystallization of secondary uranium minerals, observed paragenetic sequences in suites of such minerals and the transport and dispersion of uranium in the oxidation zone of uraniumiferous orebodies. Sufficient data has now accrued to make the last aim feasible in certain environments.

In this paper we report results concerning the stability constants of some secondary uranyl phosphate minerals and a study based on these of the solubility and transport of uranium by naturally occurring groundwaters in the oxidized zone of the Pinhal do Souto mine, northern Portugal.

Experimental

Mineral Solution Studies

H-autunite, $\text{H}_2(\text{UO}_2)_2(\text{PO}_4)_2$, its lithium, sodium and potassium analogues, autunite, $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$, saléite, $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2$, torbernite, $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2$, and its nickel analogue were prepared from the H-autunite parent compound [6] using ion-exchange techniques [7]. Numbers of water molecules of hydration are omitted for simplicity. Equilibrium solubilities for all of these minerals were determined using previously published techniques [5] in $9.31 \times 10^{-2} \text{ mol dm}^{-3}$ aqueous HClO_4 or in degassed, distilled H_2O at $298.2 \pm 0.2 \text{ K}$. Equilibrium solubilities at this temperature, being the averages of five separate determinations, are given in Table I. Numbers of water molecules of crystallization, determined thermogravimetrically using a Stanton Redcroft TG balance are also given in the Table I. X-ray powder diffraction data for all species were in agreement with published data indicating that the bulk samples were of the indicated stoichiometry [3]. An analytical check on the torbernite and autunite solutions was made, and it was found that the total

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TABLE I. Equilibrium Solubilities of the Uranium Minerals in H₂O at 298.2 K.

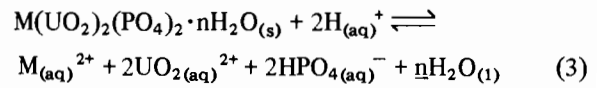
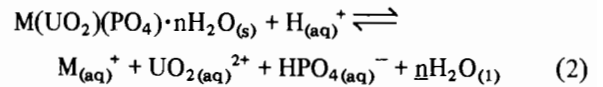
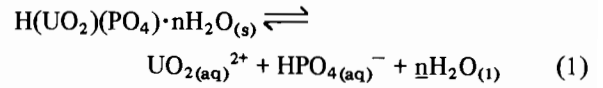
Mineral	10 ⁴ [UO ₂ ²⁺] _{TOT} / mol dm ⁻³	pH	n ^b
H-autunite ^a	8.64	2.56	4.16
Li-autunite	0.784	6.55	4.13
Na-autunite	1.48	4.95	3.45
K-autunite	0.538	5.23	2.77
Autunite ^a	4.34	2.53	6.96
Saléeite	0.482	5.64	10.25
Torbernite ^a	0.188	2.83	8.96
Ni-autunite	0.047	4.62	9.16

^aIn 9.31 × 10⁻² mol dm⁻³ aqueous HClO₄. ^bWaters of crystallization in the minerals M₂⁺/M²⁺(UO₂)₂(PO₄)₂·nH₂O (×0.5 for monovalent cation species).

Cu and Ca concentrations were one half of the uranium concentration, within experimental error.

The solubility data was used as input to the program COMICS [8] which was used to calculate the equilibrium concentrations of M_(aq)ⁿ⁺, UO_{2(aq)}²⁺ and HPO_{4(aq)}⁻. For this purpose, it was assumed that under the pH conditions of all experiments, negligible amounts of PO_{4(aq)}³⁻ were present in solution. The species taken into account (where appropriate) in the COMICS calculations were UO₂OH⁺, (UO₂)₂(OH)₂²⁺, (UO₂)₃(OH)₅⁺, (UO₂)₃(OH)₄²⁺, UO₂HPO₄⁰, UO₂-(HPO₄)₂²⁻, UO₂(H₂PO₄)₂⁰, UO₂H₂PO₄⁺, UO₂-(H₂PO₄)₃⁻, UO₂H₃PO₄²⁺, UO₂(H₃PO₄)₂²⁺, UO₂-(H₃PO₄)₃²⁺, UO₂(H₃PO₄)(H₂PO₄)⁺, UO₂(H₃PO₄)-(H₂PO₄)₂⁰, UO₂(H₃PO₄)₂(H₂PO₄)⁺, H₂PO₄⁻,

H₃PO₄⁰, LiOH⁰, LiHPO₄⁻, NaOH⁰, NaHPO₄⁻, KOH⁰, KHPO₄⁻, CaOH⁺, Ca(HPO₄)(OH)⁻[CaPO₄⁻], CaHPO₄⁰, CaH₂PO₄⁺ and the Mg(II), Cu(II), and Ni(II) analogues of the above, together with Ni₂OH³⁺, Ni(OH)₂⁰, Cu(OH)₂⁰ and Cu₂(OH)₂²⁺. For acid solution calculations, values were corrected to an ionic strength of 0.1 but for all other calculations, equilibrium constants at μ = 0 were used because of the low ionic strengths of the solutions. Full lists of constants used, the ligand being HPO₄⁻, are given in Table II**. Finally equilibrium activities of the various species were obtained using the extended form of the Debye-Huckel equation to compute individual ionic activity coefficients. Parameters used in the equation are listed in Table III**. Pertinent equilibrium data are listed in Table IV. The equilibrium constants, K_{eq}, reported in the Table refer to (1) for H-autunite, (2) for the monovalent cation minerals and (3) for the divalent cation minerals.



**These tables have been deposited with the Editor-in-Chief and are available on request.

TABLE IV. Calculated Equilibrium Data for the Secondary Uranium Phosphate Minerals at 298.2 K.

Mineral	[UO ₂ ²⁺] _e ^a	[HPO ₄ ²⁻] _e ^a	[M ⁺ /M ²⁺] _e ^a
H-autunite	2.997(-3)	1.372(-9)	
Li-autunite	4.564(-8)	2.048(-8)	7.840(-5)
Na-autunite	1.846(-5)	1.378(-9)	1.483(-4)
K-autunite	4.817(-6)	1.628(-9)	5.380(-5)
Autunite	2.533(-4)	5.307(-10)	1.428(-4)
Saléeite	1.153(-6)	3.173(-9)	2.410(-5)
Torbernite	1.386(-5)	3.625(-10)	9.400(-6)
Ni-autunite	1.751(-6)	7.615(-10)	2.350(-6)
	log γ _{UO₂²⁺}	log γ _{HPO₄²⁻}	log γ _{Mⁿ⁺}
H-autunite	-0.404	-0.432	
Li-autunite	-0.022	-0.022	-0.006
Na-autunite	-0.033	-0.033	-0.008
K-autunite	-0.020	-0.020	-0.005
Autunite	-0.404	-0.432	-0.404
Saléeite	-0.021	-0.021	-0.021
Torbernite	-0.404	-0.432	-0.404
Ni-autunite	-0.007	-0.007	-0.007
			log K _{eq} (μ = 0)
H-autunite			-12.22 ± 0.03
Li-autunite			-12.6 ± 0.1
Na-autunite			-12.5 ± 0.1
K-autunite			-13.2 ± 0.1
Autunite			-26.7 ± 0.1
Saléeite			-22.3 ± 0.1
Torbernite			-30.0 ± 0.1
Ni-autunite			-26.2 ± 0.1

^aConcentrations given thus 2.997(-3) mean 2.997 × 10⁻³ mol dm⁻³.

Field Studies

The Pinhal do Souto mine is located at the western limit of the village of Tragos near Mangualde, some 70 km east of Aveiro, Portugal. The orebody occupies a shear zone trending N34°E in a medium to fine grained alkaline granite whose primary composition consists of quartz, albite, albite-oligoclase, microperthite, muscovite, biotite, apatite and sphene. The shear/joint system is intruded in part by a lamprophyre dyke, now very altered, and is silicified in places. Alteration aside from this is typically represented by intensive (in places) kaolinization, sericitization, and the development of ferruginous impregnations and rose-coloured feldspars. Uranium mineralization is confined to this altered shear zone.

Development of the deposit, as at April, 1983, was confined to a haulage adit driven parallel to the mineralized structure, which had been intersected by a series of cross-cuts as shown in Fig. 1. Stopping had just begun at this date and no acid-leaching for the extraction of uranium by hydrometallurgical methods, a technique commonly employed in other mines of the district, had been undertaken. The minerals containing uranium in the exposed sections of the orebody are torbernite and autunite. Drilling at depth has yielded parsonite, $\text{Pb}_2\text{UO}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, phosphuranylite, $\text{Ca}(\text{UO}_2)_4(\text{PO}_4)_2(\text{OH})_4 \cdot 7\text{H}_2\text{O}$ and black uranium oxides [9].

From the point of view of the chemical studies described here the locality was ideal. The mineralized shear zone is wet, and groundwaters percolating through it can be conveniently collected (at a rate of about 1 dm^3 per hour at the time of collection) in the cross-cuts. Two sampling periods were involved in the study during September 1982 and March 1983 in order to try to take into account any seasonal variations in groundwater geochemistry. Because of the state of development of the mine at the sampling times, problems of contamination were obviated. Subsequent mining activities have introduced widespread contamination to the local groundwaters.

Groundwater samples were collected in prewashed teflon bottles at the sites shown in Fig. 1, and filtered *in situ* through a $0.45 \mu\text{m}$ Millipore® filter. Analyses were carried out immediately for $[\text{CO}_3^{2+}] + [\text{HCO}_3^-]$, by titration; temperature and pH were also measured *in situ*. A 1.5 dm^3 sample was filtered, cooled to $4 \text{ }^\circ\text{C}$, and transported to the laboratories of the Chemistry Department, University of Aveiro, where analyses for $[\text{PO}_4^{3-}]_{\text{TOT}}$, $[\text{SO}_4^{2-}]_{\text{TOT}}$, $[\text{Cl}^-]_{\text{TOT}}$, $[\text{F}^-]_{\text{TOT}}$ and $[\text{H}_4\text{SiO}_4]_{\text{TOT}}$ were carried out within 15 hours (phosphate within 12 hours). A separate filtered sample (0.5 dm^3) was acidified to pH 1 with analytical grade HNO_3 and was used to determine metal ion concentrations by AAS, except those of $[\text{UO}_2^{2+}]_{\text{TOT}}$, which were determined fluorimetrically by the staff of the Direcção Geral de Geologia e Minas, Lisboa. Except for the uranium analyses, all

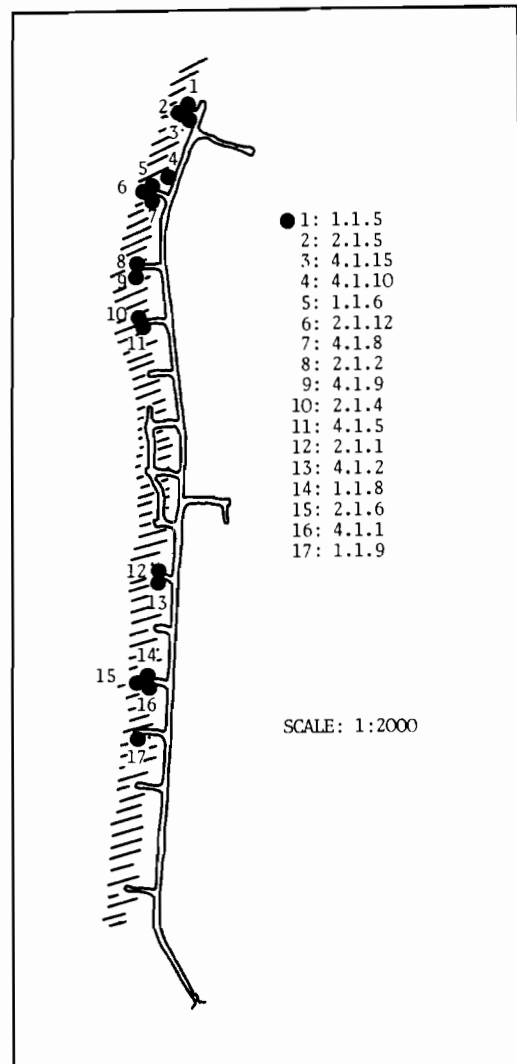


Fig. 1. Plan of haulage adit at the Pinhal do Souto mine showing locations for the groundwater samples. The approximate position of the mineralized zone is shown as the shaded area.

others were performed using the standard EPA and ASTM methods [10, 11]. Results for the groundwater analyses are given in Table V.

Equilibrium activities and species distributions for all the samples were calculated using the procedures outlined in the previous section. In all, 100 species were included in the COMICS calculations and involved constants for all of the known important species of the metals and ligands in Table V. Values taken from the literature were corrected to $15.5 \text{ }^\circ\text{C}$ where ΔH data was available, and the constants used are listed in Table VI**. Full lists of species distributions have also been deposited with the Editor-in-

**This Table has been deposited with the Editor-in-Chief and is available on request.

TABLE V. Groundwater Analyses^a from the Pinhal do Souto Orebody.

Sample No.	Cross-cut No.	pH	T/°C	Date Sampled		
1.1.9	3	5.23	14.5	13/9/82		
1.1.8	4	6.18	16.0	13/9/82		
2.1.6	4	6.18	14.4	16/9/82		
4.1.1	4	6.12	13.3	25/3/83		
2.1.1	6	5.88	14.4	16/9/82		
4.1.2	6	6.03	13.8	25/3/83		
2.1.4	11	5.85	15.2	16/9/82		
4.1.5	11	6.12	13.6	25/3/83		
2.1.2	12	5.69	15.3	16/9/82		
4.1.9	12	6.03	13.6	25/3/83		
1.1.6	13	4.49	14.6	13/9/82		
2.1.12	13	5.97	14.6	16/9/82		
4.1.8	13	6.02	14.3	25/3/83		
4.1.10	back of adit	6.08	14.0	25/3/83		
1.1.5	14	5.54	14.7	13/9/82		
2.1.5	14	5.52	14.7	16/9/82		
4.1.15	14	5.95	14.8	25/3/83		
		10^5 [Li ⁺]	10^4 [Na ⁺]	10^5 [K ⁺]	10^5 [Mg ²⁺]	10^5 [Ca ²⁺]
1.1.9		0.705	5.872	6.649	4.73	1.896
1.1.8		0.409	4.187	6.803	3.09	0.599
2.1.6		0.409	3.262	9.104	1.15	0.235
4.1.1		0.618	3.115	3.363	1.05	0.434
2.1.1		0.409	4.458	4.296	0.67	0.040
4.1.2		0.677	3.437	2.547	0.61	0.282
2.1.4		0.607	4.893	4.910	6.17	0.749
4.1.5		0.912	4.105	2.736	3.77	1.040
2.1.2		0.409	5.546	7.263	7.82	0.123
4.1.9		1.029	4.627	3.041	5.66	1.417
1.1.6		0.705	5.220	4.501	5.14	1.996
2.1.12		0.705	5.002	5.115	2.22	0.749
4.1.8		0.971	4.410	2.736	3.03	1.190
4.1.10		1.264	4.387	2.509	4.98	1.722
1.1.5		0.804	5.655	3.990	7.20	3.293
2.1.5		0.804	5.546	4.603	5.35	1.272
4.1.15		1.264	4.900	2.624	5.66	1.647
		10^8 [UO ₂ ²⁺]	10^6 [Fe ³⁺]	10^7 [Cu ²⁺]	10^5 [F ⁻]	10^4 [Cl ⁻]
1.1.9		1.39	2.78	1.90	1.84	4.118
1.1.8		0.714	4.12	1.32	1.78	3.441
2.1.6		1.09	7.70	1.90	1.55	4.287
4.1.1		1.81	0.73	0.19	0.82	3.485
2.1.1		0.882	6.45	0.16	1.78	3.695
4.1.2		1.22	0.13	0.08	1.63	2.370
2.1.4		13.86	6.80	1.32	1.74	3.103
4.1.5		3.40	0.92	2.24	1.34	2.997
2.1.2		1.72	6.09	1.32	1.71	3.695
4.1.9		2.14	0.29	1.41	1.24	3.485
1.1.6		1.43	5.01	0.74	1.73	3.216
2.1.12		1.18	9.31	1.32	2.03	3.216
4.1.8		1.64	0.24	0.41	1.11	3.415
4.1.10		1.93	0.13	0.98	1.76	3.206
1.1.5		1.47	5.37	1.32	2.29	3.216
2.1.5		1.51	7.16	2.20	2.61	3.582
4.1.15		2.35	0.62	0.63	1.82	3.555

(Continued on facing page)

TABLE V. (Continued)

Sample No.	$10^5 [\text{SO}_4^{2-}]$	$10^6 [\text{PO}_4^{3-}]^b$	$10^4 [\text{HCO}_3^-]^c$	$10^4 [\text{H}_4\text{SiO}_4^0]^d$
1.1.9	0.868	5.31	2.029	4.646
1.1.8	1.678	1.14	1.649	3.525
2.1.6	1.967	0.90	1.140	3.489
4.1.1	3.531	2.12	1.900	4.214
2.1.1	3.067	4.57	2.470	5.634
4.1.2	3.169	5.96	2.470	5.282
2.1.4	1.620	8.93	3.800	4.611
4.1.5	5.668	8.92	2.090	4.449
2.1.2	4.283	4.86	3.990	4.504
4.1.9	6.393	7.15	2.090	4.346
1.1.6	1.678	6.21	1.649	4.308
2.1.12	0.521	6.04	2.280	4.281
4.1.8	5.306	5.99	1.520	4.310
4.1.10	6.880	7.46	2.280	4.310
1.1.5	2.834	10.50	3.291	5.002
2.1.5	3.008	10.11	3.040	4.994
4.1.15	6.780	9.41	2.660	4.734

^aConcentrations given in mol dm⁻³. ^bAll phosphate species. ^c $[\text{CO}_3^{2-}]_{\text{TOT}} + [\text{HCO}_3^-]_{\text{TOT}}$. ^dAll dissolved silicate species.

Chief, as Table VII**. Individual ionic activity coefficients for the various free ions of interest were obtained using the Debye–Hückel limiting equation because of the low ionic strengths of the samples. The ionic strength was calculated from the species distribution results. Because of the low ionic strengths of the samples, it was not necessary to adjust the values of the equilibrium constants in the COMICS calculations from those reported for zero ionic strength.

Results and Discussion

Mineral Solution Studies

The value for the equilibrium constant for H-autunite (1) obtained in this work is in excellent agreement with the recent critical study of Marcović and Pavković [12] who found $\log K_{\text{eq}}$ equal to -12.33 ± 0.06 at $\mu = 0$ and 298.15 K. This result is of some importance to the field studies reported below in that the quality of the set of equilibrium constants for phosphate containing species is reliable for calculating the concentration of free uranyl ion even if the precision of the calculated complexed species is somewhat dependent upon the magnitudes of the constants employed. Similarly, the values reported for the alkali metal and alkaline earth autunite analogues are in good agreement with values listed in the comprehensive compilation of data collected by Langmuir [2] when the correction is made to Muto *et al.*'s value for the free energy of forma-

tion of H-autunite [7]. In addition, the results for torbernite and the other two transition metal analogues closely agree with the recent determination of Vochten *et al.*, [3].

As far as the field studies are concerned, it is critical that as accurate values for the equilibrium constants as possible are available. This applies particularly to the data for autunite and torbernite, in connection with the Pinhal do Souto deposit. The close correspondence between the various sets of data published by a number of groups with our results give us confidence to apply the findings to problems involving natural aqueous systems.

Field Studies

From the analytical data reported in Table V it is seen that little variation in groundwater geochemistry in the mineralized shoot at the Pinhal do Souto mine is evident over the period of the two sampling times chosen. Except in one case, the uranium concentrations in the samples are reasonably constant, as are the concentrations of all other ions and physical parameters measured. While these analytical results themselves are not particularly revealing with respect to mobilization of uranium in the circulating groundwaters of the deposit or crystallization of various secondary minerals, some noteworthy features of the groundwater geochemistry in the mineralized zone containing torbernite and autunite are evident from the species distribution calculations.

Table VIII gives selected relevant equilibrium concentrations and thermodynamic parameters calculated for the groundwater samples. A general relationship is seen for the sympathetic variation

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TABLE VIII. Relevant Equilibrium Concentrations^a for Selected Species and Calculated Thermodynamic Parameters^b for the Pinhal do Souto Groundwater Samples.

Sample No.	$10^4 I^a$	$10^7 [Cu^{2+}]$	$10^5 [Ca^{2+}]$	$10^{12} [UO_2^{2+}]$
1.1.5	7.72	1.312	3.273	0.641
1.1.6	6.68	0.739	1.989	200.0
1.1.8	5.65	1.275	0.597	1.592
1.1.9	7.10	1.897	1.892	9.594
2.1.1	5.48	0.154	0.040	0.444
2.1.2	7.87	1.305	0.122	1.797
2.1.4	6.53	1.295	0.746	2.216
2.1.5	7.12	2.187	1.264	0.777
2.1.6	5.01	1.847	0.234	3.973
2.1.12	5.55	1.292	0.748	0.299
4.1.1	4.88	0.183	0.431	1.528
4.1.2	4.36	0.076	0.280	0.187
4.1.5	6.30	2.159	1.028	0.161
4.1.8	6.30	0.409	1.178	0.262
4.1.9	7.34	1.371	1.399	0.231
4.1.10	7.17	0.953	1.699	0.155
4.1.15	7.70	0.615	1.625	0.208

	$10^7 [HPO_4^{2-}]$	γ_{\pm}	$\gamma_{2\pm}$	$\log K_{TORB}'$	$\log K_{AUT}'$
1.1.5	2.136	0.968	0.879	-33.8	-31.4
1.1.6	0.114	0.971	0.890	-33.7	-31.3
1.1.8	0.939	0.973	0.896	-32.4	-30.8
1.1.9	0.534	0.970	0.884	-33.1	-31.1
2.1.1	1.989	0.973	0.897	-34.4	-33.0
2.1.2	1.380	0.968	0.878	-33.0	-32.0
2.1.4	3.530	0.971	0.888	-31.7	-29.9
2.1.5	1.968	0.970	0.884	-33.5	-31.8
2.1.6	0.734	0.974	0.902	-31.7	-30.6
2.1.12	3.198	0.973	0.897	-33.5	-31.7
4.1.1	1.531	0.975	0.903	-33.0	-30.6
4.1.2	3.598	0.976	0.908	-34.6	-32.1
4.1.5	6.497	0.971	0.890	-32.6	-31.0
4.1.8	3.529	0.971	0.890	-33.7	-31.2
4.1.9	4.295	0.969	0.882	-33.1	-31.1
4.1.10	4.993	0.969	0.883	-33.4	-31.1
4.1.15	4.753	0.968	0.879	-33.6	-31.2

^a Equilibrium concentration in mol dm⁻³. ^b $K_{TORB}' = a_{Cu^{2+}} a_{UO_2^{2+}}^2 a_{HPO_4^{2-}}^2 / a_{H^+}^2$; $K_{AUT}' = a_{Ca^{2+}} a_{UO_2^{2+}}^2 a_{HPO_4^{2-}}^2 / a_{H^+}^2$.

involving rising $[UO_2^{2+}]_e$ with decreasing pH. This result is entirely to be expected; pH has always been viewed as a prime variable with respect to the control of uranium concentrations in natural aqueous solutions [1–5, 13]. Of particular interest are the values of the computed ionic activity products for expressions related to the equilibrium constants for torbernite and autunite as given in (3). In all cases, the values for solutions from the Pinhal do Souto orebody show that the groundwaters are undersaturated with respect to these two minerals by some 2 to 4 orders of magnitude. These vast discrepancies could not be accounted for by temperature variations.

The clear conclusion that can be drawn from these field studies is that, at the Pinhal do Souto deposit,

groundwaters are considerably undersaturated with respect to autunite and torbernite. In other words, the two minerals are actively dissolving. This conclusion in turn leads to others concerning the deposit in terms of the deposition of the secondary minerals and dispersion of uranium from the deposit. First, it is obvious that the secondary species crystallized from aqueous solutions of quite different compositions than those currently circulating in the mineralized zone. It is possible that the secondary phosphate minerals were deposited by late-stage, hot (or at least warm) aqueous fluids, associated with the remnants of solutions responsible for the granite emplacement. Secondly, it is certain that uranium is being dispersed from the ore zone by present day

TABLE IX. Selected Equilibrium Data^a for the Groundwater Samples for the Kaolinite Stability Field Plot of Fig. 2.

Sample No.	$10^4 a_{\text{H}_4\text{SiO}_4^0}$	γ_{Na^+}	$10^4 a_{\text{Na}^+}$	$a_{\text{H}_4\text{SiO}_4^0}$	pH - pNa
1.1.5	5.002	0.968	5.473	3.30	2.28
1.1.6	4.308	0.971	5.069	3.37	1.19
1.1.8	3.524	0.973	4.074	3.45	2.79
1.1.9	4.646	0.970	5.696	3.33	1.99
2.1.1	5.633	0.973	4.337	3.25	2.52
2.1.2	4.504	0.968	5.368	3.35	2.42
2.1.4	4.611	0.971	4.750	3.34	2.53
2.1.5	4.994	0.970	5.379	3.30	2.25
2.1.6	3.488	0.974	3.275	3.46	2.70
2.1.12	4.280	0.973	4.867	3.37	2.66
4.1.1	4.213	0.975	3.036	3.38	2.60
4.1.2	5.281	0.976	3.354	3.28	2.56
4.1.5	4.448	0.971	3.985	3.35	2.72
4.1.8	4.309	0.971	4.281	3.37	2.65
4.1.9	4.345	0.969	4.482	3.36	2.68
4.1.10	4.309	0.969	4.249	3.37	2.71
4.1.15	4.733	0.968	4.741	3.32	2.63

^a $\gamma_{\text{H}_4\text{SiO}_4^0}$ taken to be equal to unity.

groundwaters. Thus aqueous geochemical methods may be of considerable application to exploration geochemical techniques in the search for new ore-bodies in similar environments in northern Portugal and along extensions to known uraniferous mineralized structures.

A comment is also warranted concerning the relationships found for the solutions with respect to their general setting. Kaolinization of the ore shoot is a recognised feature of the Pinhal do Souto deposit. Previous workers [14] have reported stability diagrams for a number of feldspars, micas and clays. Accordingly, we have plotted data concerning the field samples on the diagram shown in Fig. 2. Data from COMICS calculations for the plot are gathered together in Table IX. The consistency of the plot with field observations as shown in the Fig. 2 also lends support to the fitness of the kinds of calculations carried out here to describe the geochemical relationships outlined above.

We conclude that a thermodynamic approach to the dispersion of uranium in the natural environment is of value in understanding the chemical processes occurring. We do not claim, of course, that equilibrium necessarily exists in such systems. Nor do we claim that the only species involved are those dissolved in aqueous solution, together with solid mineral phases. Many other controls on the concentrations of metal ions in natural solutions are known to be important [14]. We do maintain, however, that the simple thermodynamic approach, embodied in a model such as that outlined above, and notably by other workers [13], can give valuable chemical insights into the transportation and immobilization of metal ions, in this instance UO_2^{2+} , in circulating near-surface groundwaters.

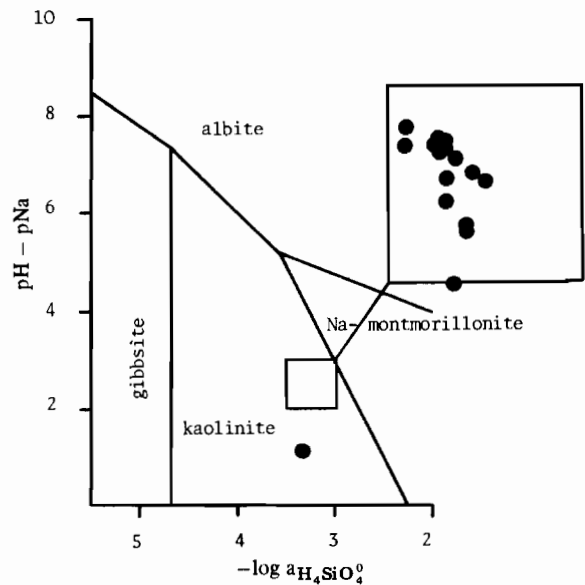


Fig. 2. Plot of selected groundwater equilibrium data for the samples on the kaolinite stability field. Data are taken from Table IX.

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