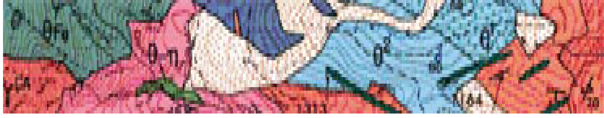

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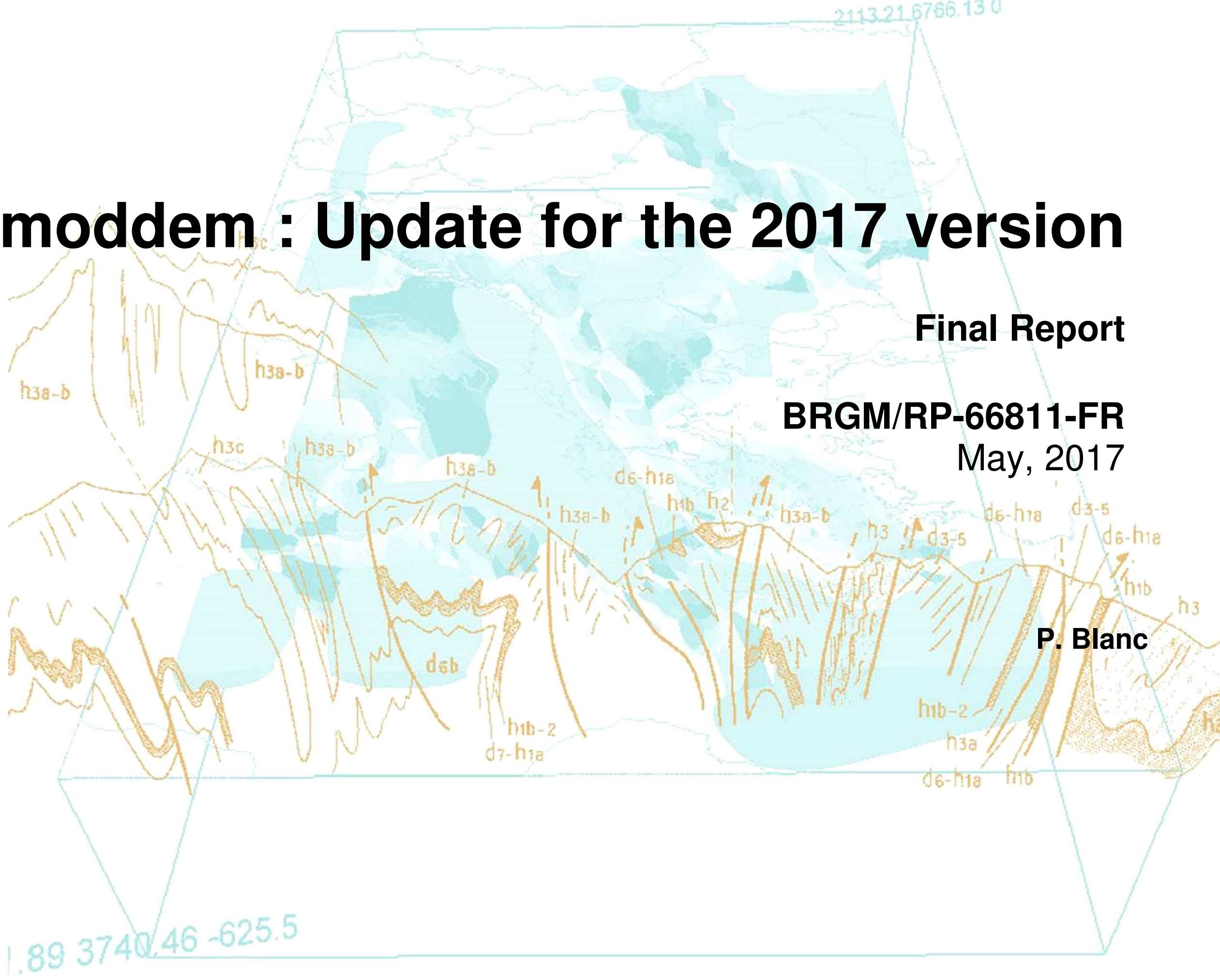

Thermoddem : Update for the 2017 version

Final Report

BRGM/RP-66811-FR
May, 2017

P. Blanc

Geoscience for a sustainable Earth
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Study carried out as part of Public Service (or Research) activities - BRGM 2017 – Project Thermoddem

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Synopsis

The document reports a suite of actions carried out during 2016, within the course of a Brgm internal project supporting the development of Thermoddem database. The different actions include:

- The re-assessment of the properties of Microcline, Albite, Anorthite, Prehnite, Zoisite, Clinozoisite and Epidote (Thank to N. Spycher LBNL) and F/CO_3 apatites (thank to David Shafer, UWA University, Australia)

- The estimation of S° and Cp for aqueous complexes using the isocoulombic method, to complete the thermodynamic datasets in the SiO_2-Al_2O_3-Fe_2O_3-FeO-CaO-Na_2O-K_2O-MgO-CO_2-S-Cl-H_2O chemical system.

In addition, the 2017 release is also the results of actions carried out during the 2014-2016 period:

- An updated selection for thallium (thanks to the Transmob project, BRGM intern funding)

- a selection for copper (thanks to the E.U. funded project Biomore).

Mineral families groups have been re-assessed for sake of simplicity

Finally, a surface complexation dataset is now provided (thanks to N. Devau and A. Lassin, BRGM).

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1. Introduction: context and needs

The need to stabilize the database at high temperature (200 to 300°C) arises especially from projects and partners related to the geothermal field. The improvements proposed in this note is in line with E.U. funded project, GeoWell, whose main objective is to develop and test reliable, cost effective and environmentally safe completion and monitoring technologies for geothermal wells. Focus will be on high-temperature geothermal well technologies, as this is needed to accelerate the development of geothermal resources for power generation both in Europe and worldwide. The chemical durability of the cement casing is planned to be investigated especially using geochemical calculations. This requires reviewing, homogenizing and improving the database concerning the high temperature properties. In addition to the different selection and estimation works, a specific testing case is considered here, the Wairakei geothermal field, previously investigated by Bruton (1995), in line with issues under studies at the LBNL (N. Spycher pers. com.).

The present document includes a critical review focused on major elements (system SiO_2-Al_2O_3-Fe_2O_3-FeO-CaO-Na_2O-K_2O-MgO-CO_2-S-Cl-H_2O). The aim is to update the database in this system, focusing the work on the high temperature properties. When required thermodynamic properties have been estimated using the isocoulombic/isoelectric approach (Gu et al., 1994). The update concerns both aqueous complexes and a selection of minerals of interest.

2. Aqueous complexes (system SiO_2-Al_2O_3-Fe_2O_3-FeO-CaO-Na_2O-K_2O-MgO-CO_2-S-Cl-H_2O)

In table 1 are reported a list of the aqueous complexes which have been modified in this work. The modification arises from different issues:

- an update necessary after the publication of a selection for iron-bearing compounds (Lemire et al., 2013)
- a re-assessment of the Na-carbonates complexes properties
- the removal of quite rare and difficult to constrain complexes (sulfites)
- the completion of thermodynamic datasets by estimates, especially for silicates.

An important update had been realized by considering a recent selection for iron bearing compounds proposed by Lemire et al. (2013). The review was used in order to select or to remove some questionable species, especially for sulfate and carbonate complexes. In addition, the selection allows integrating more accurate and more significant values for the entropies of some complexes (chlorides). The list of the complexes concerned and the nature of the modification are given in tables 1 and 2. The re-assessment for carbonates is based on the recent study proposed by Grivé et al. (2014).

Concerning Na-carbonate complexes, a recent potentiometric study by Stefansson et al. (2013) has succeeded in providing reliable entropy values, the equilibrium constant being found consistent with this recent contribution, within uncertainty limits. The Cp(298.15 K) values are considered constants and calculated considering that $\Delta_r Cp = 0$ J/mol.K, according to Stefansson et al. (2013).

The removal of some complexes results from various considerations. The aim is generally to discard the complexes whose presence is questionable:

- Fe-sulfates: our previous selection was essentially based on works proposed by Cifuentes et al. (2006). These have been reviewed recently by Lemire et al. (2013) and lead to consider a different list of complexes than previously selected in Thermoddem (Blanc, 2008).
- Fe-carbonates: Lemire et al. (2013) have proposed an improved list of carbonate-iron complexes. For Iron III, it is based on the recent study from Grivé et al. (2014) on ferrihydrite solubility. We have retained this selection.
- $BaCO_3$: this aqueous complex was reported twice in the Thermoddem database because of typing issues. The specie $Ba(CO_3)$ is now removed from the database.
- Sulfites: The Mg complex stability is based on a single measurement and the Na-complex is from the Wagman et al. (1982) selection, the experimental source is difficult to trace.
- Mg-Si and Ca-Si complexes. Na-Si complexes were already discarded, based on a discussion held by Busey and Mesmer (1977). The Ca-Si and Mg-Si complexes are relying on a single study by Santschi and Schindler (1974) and hypotheses proposed by the authors. Precipitation of solids is reported by the authors. Finally, these complexes are dominant for pH > 9, that is out of the domain covered by the experiments. For all these reasons, the mixed Si complexes are not selected for the database.

To complete the thermodynamic datasets, the isocoulombic/isoelectric method, illustrated by Gu et al. (1994), is implemented. The success of the method is growing (Xiong, 2009) and the present work was offering the opportunity to test it. In Table 1 is reported the isocoulombic/isoelectric reaction considered. In Table 2 are reported the properties estimated, S° (298.15 K) and/or Cp (298.15 K) and the value obtained. An important issue here is the nature of the reaction used in order to complete the considered complex equilibrium. No guidelines are provided, for example by Gu et al. (1994). We have favored reaction exchanging ligands, using the same metal than which forming the complex of interest. The results are provided on Table 2. It has to be said that very different results would have been obtained if choosing different sets of reactions. The test on the Wairakei field is a way to verify the selection. However, the estimates using the isocoulombic approach appear strongly related to the guidelines followed in selecting the complementary reaction.

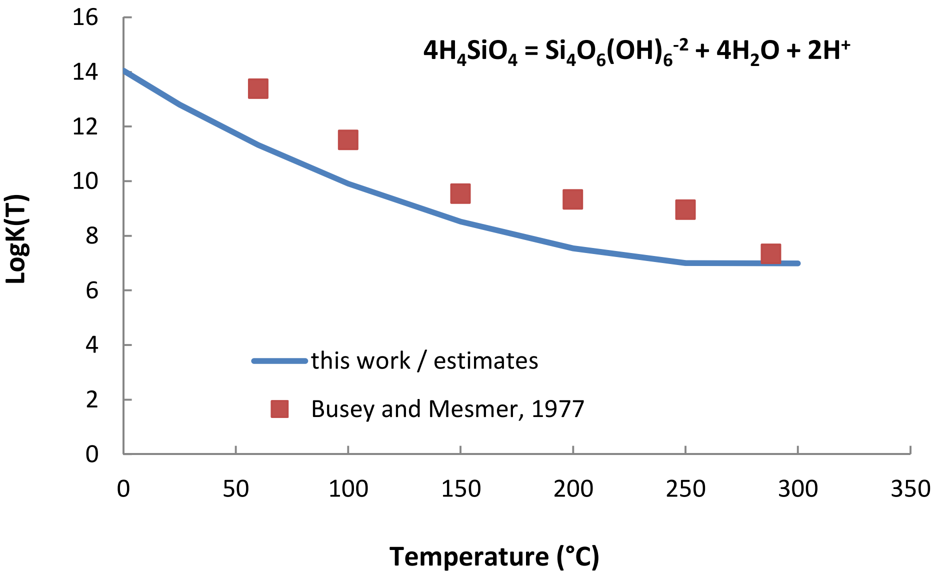

Figure 1 - Equilibrium constant of the $Si_4O_6(OH)_6^{-2}$ complex

A limited verification could be done when considering the potentiometry study of polysilicate complexes by Busey and Mesmer (1977), up to 300°C. From this study, the main polynuclear silica complex appears to be $Si_4O_6(OH)_6^{-2}$. Its formation constant is represented on Figure 1, after Busey and Mesmer (1977) data. The evolution is quite well reproduced with the estimates of S° and Cp calculated here by using the isocoulombic reaction $2H_4SiO_4 + Si_2O_3(OH)_4^{-2} = Si_4O_6(OH)_6^{-2} + 3H_2O$. In addition, the speciation diagrams provided by the authors can be compared on Figure 2 with the diagrams calculated using the whole silica speciation updated in Thermoddem and the GWB code (Bethke et al., 2004). The transitions for the mononuclear species are quite well reproduced. The situation is less clear for the polynuclear species at Si=0.02 M. This concentration is quite high for the systems of interest in our case and the issue appears at 25°C. Our selection for polynuclear species (Blanc et al., 2006) considers other and more recent studies (Felmy et al., 2001), which explains the discrepancies. In all cases, discrepancies are not specifically related to the S° (298.15 K) and Cp (298.15 K) estimates.

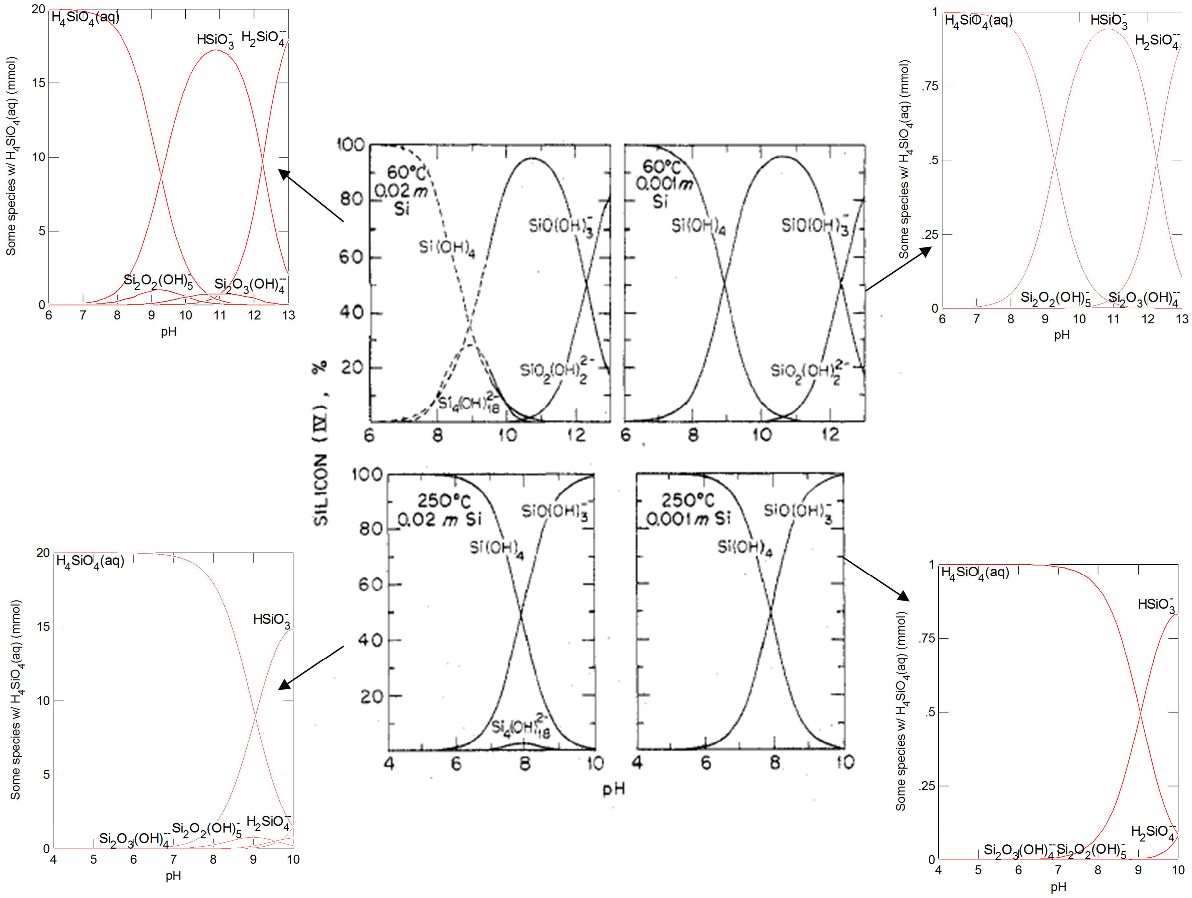

Figure 2 - Sillén diagrams of the silica speciation for 2 temperatures and 2 silica concentrations.

The original diagrams from Busey and Mesmer (1977) are located in the center and the GWB calculations are surrounding these latter.

Table 1 - List of aqueous complexes modified in this work

Complex	Equilibrium reaction in Thermoddem	Isocoulombic / Isoelectric reaction	Additional complex	Comments
$Fe_2(OH)_2^{+4}$	2Fe+++ + 2H2O = Fe2(OH)2+4 + 2H+	2Fe(OH)+2 = Fe2(OH)+4	Fe(OH)+2	Assessed vs 13lem/ber
$FeSO_{4,aq}$	1Fe+2 + 1SO4-2 = FeSO4	FeCl2 + SO4-2 = FeSO4 + 2Cl-	FeCl2	Assessed vs 13lem/ber
$FeHSO_4^+$	1Fe+2 + 1SO4-2 + 1H+ = FeHSO4+	FeCl+ + HSO4- = FeHSO4+ + Cl-	FeCl+	Assessed vs 13lem/ber
$FeSO_4^+$	1Fe+3 + 1SO4-2 = FeSO4+	FeCl2+ + SO4- = FeSO4+ + 2CL-	FeCl2+	Assessed vs 13lem/ber
$FeHSO_4^{++}$	1Fe+3 + 1SO4-2 + 1H+ = FeHSO4+2	FeCl+2 + HSO4- = FeHSO4+2 + Cl-	FeCl+2	Assessed vs 13lem/ber
$Fe(HS)_{2,aq}$	1Fe+2 + 2HS- = Fe(HS)2	FeCl2 + 2HS- = Fe(HS)2 + 2Cl-	FeCl2	Assessed vs 13lem/ber
$FeCO_3OH_{aq}$	1HCO3- + 1Fe+3 + 1H2O = FeCO3OH + 2H+	HFeO2 + CO2 = FeCO3OH	HFeO2	New complex 13lem/ber
$Fe(CO_3)_3^{-3}$	3HCO3- + 1Fe+3 = Fe(CO3)3-3 + 3H+	Fe+3 + 3HCO3- = Fe(CO3)3-3 + 3H+		New complex 13lem/ber
$FeCO_{3,aq}$	1HCO3- + 1Fe+2 = FeCO3 + 1H+	FeCl2 + CO3-2 = FeCO3 + 2Cl-	FeCl2	Assessed vs 13lem/ber
$Fe(CO_3)_2^{-2}$	2HCO3- + 1Fe+2 = Fe(CO3)2-2 + 2H+	FeCl2 + 2CO3-2 = Fe(CO3)2-2 + 2Cl-	FeCl2	Assessed vs 13lem/ber
$Fe(CO_3)_2^-$	2HCO3- + 1Fe+3 = Fe(CO3)2- + 2H+			Suppressed
$FeHCO_3^+$	1HCO3- + 1Fe+2 = FeHCO3+			Suppressed
$FeCO_3^+$	1HCO3- + 1Fe+3 = FeCO3+ + 1H+			Suppressed
$FeCO_3OH^-$	1HCO3- + 1Fe+2 + 1H2O = FeCO3OH- + 2H+			Suppressed
$Fe(SO_4)_2^-$	1Fe+3 + 2SO4-2 = Fe(SO4)2-			Suppressed
$Fe_2(SO_4)_{3,aq}$	2Fe+3 + 3SO4-2 = Fe2(SO4)3			Suppressed
$FeH(SO_4)_{2,aq}$	1Fe+3 + 2SO4-2 + 1H+ = FeH(SO4)2			Suppressed
$FeCl_{2,aq}$	2Cl- + 1Fe+2 = FeCl2			Assessed vs 13lem/ber
$FeCl^+$	1Cl- + 1Fe+2 = FeCl+			Assessed vs 13lem/ber
$FeCl^{++}$	1Cl- + 1Fe+3 = FeCl++			Assessed vs 13lem/ber
$FeCl_2^+$	2Cl- + 1Fe+3 = FeCl2+	FeCl+2 + CaCl+ = Ca+2 + FeCl2+	CaCl+	Assessed vs 13lem/ber
$NaCO_3^-$	1HCO3- + 1Na+ = NaCO3- + 1H+			13ben/ste

$NaHCO_3^-$	1HCO3- + 1Na+ = NaHCO3			13ben/ste
$Mg_4(OH)_4^{+4}$	4Mg+2 + 4H2O = Mg4(OH)4+4 + 4H+	4Mg(OH)+ = Mg4(OH)4+4	Mg(OH)+	Completed with estimates
$NaS_2O_3^-$	1Na+ + 1S2O3-2 = NaS2O3-			Suppressed
$MgS_2O_{3,aq}$	1Mg+2 + 1S2O3-2 = MgS2O3			Suppressed
$Ba(CO_3)_{aq}$	1Ba+2 + 1HCO3- = Ba(CO3) + 1H+			Suppressed
$CaSiO(OH)_3^+$	1Ca+2 + 1H4SiO4 = CaSiO(OH)3+ + 1H+			Suppressed
$CaSiO_2(OH)_{2,aq}$	1Ca+2 + 1H4SiO4 = CaSiO2(OH)2 + 2H+			Suppressed
$NaHSiO_{3,aq}$	1Na+ + 1H4SiO4 = NaHSiO3 + 1H2O + 1H+			Suppressed
$MgSiO(OH)_3^+$	1Mg+2 + 1H4SiO4 = MgSiO(OH)3+ + 1H+			Suppressed
$MgSiO_2(OH)_{2,aq}$	1Mg+2 + 1H4SiO4 = MgSiO2(OH)2 + 2H+			Suppressed
$H_2SiO_2^{--}$	1H4SiO4 = H2SiO4-2 + 2H+	HSiO3- + OH-= H2SiO4--	OH-	Completed with estimates
$Si_2O_2(OH)_5^-$	2H4SiO4 = Si2O2(OH)5- + 1H2O + 1H+	H4SiO4 + HSiO3- = Si2O2(OH)5-	HSiO3-	Completed with estimates
$Si_2O_3(OH)_4^{-2}$	2H4SiO4 = Si2O3(OH)4-2 + 1H2O + 2H+	2HSiO3- + H2O = Si2O3(OH)4-2	HSiO3-	Completed with estimates
$Si_3O_5(OH)_5^{-3}$	3H4SiO4 = Si3O5(OH)5-3 + 2H2O + 3H+	HSiO3- + Si2O3(OH)4-2 = Si3O5(OH)5-3	HSiO3- / Si2O3(OH)4-2	Completed with estimates
$Si_3O_6(OH)_3^{-3}$	3H4SiO4 = Si3O6(OH)3--- + 3H2O + 3H+	HSiO3- + Si2O3(OH)4-2 = Si3O6(OH)3-3 + H2O	HSiO3- / Si2O3(OH)4-2	Completed with estimates
$Si_4O_{12}H_4^{-4}$	4H4SiO4 = Si4O12H4-4 + 4H2O + 4H+	HSiO3- + Si3O6(OH)3-3 = Si4O12H4-4	HSiO3- / Si3O6(OH)3-3	Completed with estimates
$Si_4O_6(OH)_6^{-2}$	4H4SiO4 = Si4O6(OH)6-2 + 4H2O + 2H+	2H4SiO4 + Si2O3(OH)4-2 = Si4O6(OH)6-2 + 3H2O	H4SiO4 / Si2O3(OH)4-2	Completed with estimates
$Si_4O_7(OH)_5^{-3}$	4H4SiO4 = Si4O7(OH)5-3 + 4H2O + 3H+	Si3O6(OH)3-3 + H4SiO4 = Si4O7(OH)5-3 + H2O	H4SiO4 / Si3O6(OH)3-3	Completed with estimates
$Si_4O_7(OH)_6^{-4}$	4H4SiO4 = Si4O7(OH)6-4 + 3H2O + 4H+	Si3O5(OH)5-3 + HSiO3- = Si4O7(OH)6-4	HSiO3- / Si3O5(OH)5-3	Completed with estimates
$Si_4O_8(OH)_4^{-4}$	4H4SiO4 = Si4O8(OH)4-4 + 4H2O + 4H+	Si3O6(OH)3-3 + HSiO3- = Si4O8(OH)4-4	HSiO3- / Si3O6(OH)3-3	Completed with estimates
$Si_6O_{15}^{-6}$	6H4SiO4 = Si6O15-6 + 9H2O + 6H+	Si4O12H4-4 + 2HSiO3- = Si6O15-6 + 3H2O	Si4O12H4-4 / HSiO3-	Completed with estimates

Table 2 - Re-assessment, completion of the thermodynamic datasets for aqueous complexes

Complex	**LogK°**	**ΔG^0_f (J/mol)**	**ΔH^0_f (J/mol)**	**S^0 (J/mol.K)**	**Cp° (J/mol.K)**	**References / comments**
$Fe_2(OH)_2^{+4}$	-2.92	-490173	-613180	-283.45	-68.62	ΔHr 76bae/mes ; Cp° estimated
$FeSO_{4,aq}$	2.44	-848462	-990940	-8.20	-75.12	S°, Cp estimated
$FeHSO_4^+$	1.74	-844466	-989440	-16.57	163.39	S°, Cp estimated
$FeSO_4^+$	4.25	-784544	-932340	-91.37	-273.96	S°, Cp estimated
$FeHSO_4^{+2}$	2.48	-774440	-883065	40.01	-68.60	S°, Cp estimated
$Fe(HS)_{2,aq}$	6.45	-102861	-159449	32.31	99.31	S°, Cp estimated
$FeCO_3OH_{aq}$	-9.97	-783357	-907335	92.9	-312.12	S°, Cp estimated
$Fe(CO_3)_3^{-3}$	-11.68	-625846	-689996	217.38	-384.64	S°, Cp estimated
$FeCO_{3,aq}$	-9.82	-1016033	-1146115	20.92	-81.50	ΔHr 84fou/cri ; confirmed by Lemire et al. (2013)
$Fe(CO_3)_2^{-2}$	-6.99	-1736917	-2019075	-201.69	-349.35	S°, Cp estimated
$FeCl_{2,aq}$	-1.74	-343035	-414260	11.51	120.71	ΔHr 01zha/pan ; confirmed by Lemire et al. (2013) ; Cp 97sve/sch
$FeCl^+$	-0.16	-220835	-235530	24.23	89.06	ΔHr 13lem/ber ; Cp 97sve/sch
$FeCl^{+2}$	1.52	-156175	-193600	-117.35	21.08	ΔHr 13lem/ber; Cp 97sve/sch
$FeCl_2^+$	0.70	-282712	-360980	-77.45	-76.67	ΔHr 13lem/ber ; Cp 97sve/sch
$NaCO_3^-$	-9.06	-797101	-897818	92.30	-289.69	13ste/ben, Cp estimated
$NaHCO_3^-$	-0.25	-847388	-918291	192.30	-34.30	13ste/ben, Cp estimated
$Mg_4(OH)_4^{+4}$	-39.75	-2543168	-2782134	-260.51	515.50	Cp estimated
$H_2SiO_2^{-2}$	-23.27	-1176400	-1386194	-13.18	-238.04	Cp estimated
$Si_2O_2(OH)_5^-$	-8.50	-2332794	-2614844	201.69	150.14	S°, Cp estimated
$Si_2O_3(OH)_4^{-2}$	-19.40	-2270576	-2579430	111.79	-100.38	S°, Cp estimated
$Si_3O_5(OH)_5^{-3}$	-29.40	-3285582	-3724518	132.71	-188.24	S°, Cp estimated
$Si_3O_6(OH)_3^{-3}$	-29.40	-3048441	-3438688	62.76	-263.59	S°, Cp estimated
$Si_4O_{12}H_4^{-4}$	-39.20	-4064589	-4584918	83.68	-351.46	S°, Cp estimated
$Si_4O_6(OH)_6^{-2}$	-15.20	-4201581	-4668303	263.48	159.57	S°, Cp estimated
$Si_4O_7(OH)_5^{-3}$	-25.50	-4142788	-4615458	243.53	-20.59	S°, Cp estimated

Complex	**LogK°**	**ΔG^0_f (J/mol)**	**ΔH^0_f (J/mol)**	**S^0 (J/mol.K)**	**Cp° (J/mol.K)**	**References / comments**
$Si_4O_7(OH)_6^{-4}$	-39.10	-4302300	-4871318	153.63	-276.11	S°, Cp estimated
$Si_4O_8(OH)_4^{-4}$	-39.10	-4065159	-4585488	83.68	-351.46	S°, Cp estimated
$Si_6O_{15}^{-6}$	-61.50	-5370050	-6004475	-84.33	-753.23	S°, Cp estimated

Table 3 - Additional complexation reactions considered to implement the isocoulombic/isoelectric method. Data stemming from Thermoddem

Complex	Equilibrium reaction	LogK°	ΔG^0_f (J/mol)	ΔH^0_f (J/mol)	S^0 (J/mol.K)	Cp° (J/mol.K)	References / comments
$FeOH^{+2}$	1Fe+3 + 1H2O = FeOH+2 + 1H+	-2.19	-240920	-298927	-130.00	-28.41	Blanc et al. 2012
$FeCl_{2,aq}$	2Cl- + 1Fe+2 = FeCl2	-1.74	-343035	-414260	11.51	120.71	Blanc et al. 2012
$FeCl^+$	1Cl- + 1Fe+2 = FeCl+	-0.16	-220835	-235530	24.23	89.06	Blanc et al. 2012
$FeCl_2^+$	2Cl- + 1Fe+3 = FeCl2+	0.70	-282712	-360980	-77.45	-76.67	Blanc et al. 2012
$FeCl^{+2}$	1Cl- + 1Fe+3 = FeCl+2	1.52	-156175	-193600	-117.35	21.08	Blanc et al. 2012
$HFeO_{2,aq}$	1Fe+3 + 2H2O = HFeO2 + 3H+	-14.30	-408936	-470035	92.88	-313.28	Blanc et al. 2012
$CaCl^+$	1Ca+2 + 1Cl- = CaCl+	-0.29	-682369	-702930	18.83	75.09	Blanc et al. 2012
$MgOH^+$	1Mg+2 + 1H2O = MgOH+ + 1H+	-11.68	-625846	-689996	-79.91	132.33	Blanc et al. 2012
$HSiO_3^-$	1H4SiO4 = HSiO3- + 1H2O + 1H+	-9.82	-1016033	-1146115	20.92	-81.50	Blanc et al. 2012
$H_4SiO_{4,aq}$	H4SiO4 = H4SiO4	0.00	-1309226	-1461194	180.77	243.28	Refined in this work
OH^-	1H2O = OH- + 1H+	-14.00	-157220	-230015	-10.90	-130.00	CODATA

Table 4 - List of the minerals re-assessed in the frame work of the present document. In bold characters, new selection.

Mineral	Equilibrium reaction	ΔG^0_f (J/mol)	ΔH^0_f (J/mol)	S^0 (J/mol.K)	Cp° (J/mol.K) (1)	V (cm^3/mol)	References
Microcline	K(AlSi3)O8 + 4H+ + 4H2O = 1Al+3 + 1K+ + 3H4SiO4	-3748993	-3974340	214.20	202.13	108.74	n/a ; 06bla/pia ; 06bla/pia ; 06bla/pia ; 78hel/del
		-3749253	**-3974600**	**214.20**	**202.20**	**108.72**	**95rob/hem**
Albite	NaAlSi3O8 + 4H+ + 4H2O = 1Al+3 + 1Na+ + 3H4SiO4	-3713043	-3936190	208.20	260.44	100.07	n/a ; 06bla/pia ; 06bla/pia ; 06bla/pia ; 78hel/del
		-3711615	**-3935000**	**207.40**	**205.14**	**100.07**	**95rob/hem**
Anorthite	Ca(Al2Si2)O8 + 8H+ = 2Al+3 + 1Ca+2 + 2H4SiO4	-4002095	-4227830	199.30	50.47	100.79	n/a ; 06bla/pia ; 06bla/pia ; 06bla/pia ; 78hel/del,92ajoh
		-4008265	**-4234000**	**199.30**	**211.34**	**100.79**	**95rob/hem**
Prehnite	Ca2Al2Si3O10(OH)2 + 10H+ = 2Al+3 + 2Ca+2 + 3H4SiO4	-5826000	-6202600	292.80	330.57	141.10	95rob/hem
		-5816471	**-6199766**	**292.80**	**330.57**	**141.10**	**n/a ; 98cha/kru ; 95rob/hem ; 95rob/hem ; 95rob/hem**
Zoisite	Ca2Al3Si3O12(OH) + 13H+ = 3Al+3 + 2Ca+2 + 3H4SiO4 + 1H2O	-6481451	-6877203	295.98	347.69	135.90	78hel/del,92ajoh
		-6483166	**-6878500**	**297.38**	**350.90**	**135.72**	**n/a ; 01sme/fra ; 04got ; 04got ; 04got**
Clinozoisite	Ca2Al3Si3O12(OH) + 13H+ = 3Al+3 + 2Ca+2 + 3H4SiO4 + 1H2O	-6482020	-6877898	295.56	347.69	136.20	78hel/del
		-6494260	**-6890340**	**294.88**	**347.69**	**136.40**	**04got**
Epidote	Ca2FeAl2Si3O12(OH) + 13H+ = 2Al+3 + 2Ca+2 + 1Fe+3 + 3H4SiO4 + 1H2O	-6070591	-6460388	314.97	358.14	139.20	78hel/del,92ajoh
		-6078118	**-6462600**	**332.80**	**362.89**	**139.01**	**04got**

(1) With Maier-Kelley coefficients

3. Minerals of interest in the SiO_2-Al_2O_3-Fe_2O_3-CaO-Na_2O-K_2O-H_2O system, verification using a geothermal case

The re-assessment of the whole mineral list would be quite time consuming and not always necessary, depending on the minerals. Helped with discussions with N. Spycher (LBNL) and focusing on the Wairakei verification case, we could restrain the list to the following phases: Microcline, Albite, Anorthite, Prehnite, Zoisite, Clinozoisite and Epidote. The former and the new thermodynamic properties are reported on Table 4. Globally, we have adopted the properties proposed by Robie and Hemingway (1995). For Zoisite, Clinozoisite and Epidote, we have preferred a more recent and very complete review realized by Gottschalk (2004). An illustration of those modifications is given in Figure 3. The new selection, for both microcline and albite allows joining the group of curves generally predicted using different databases.

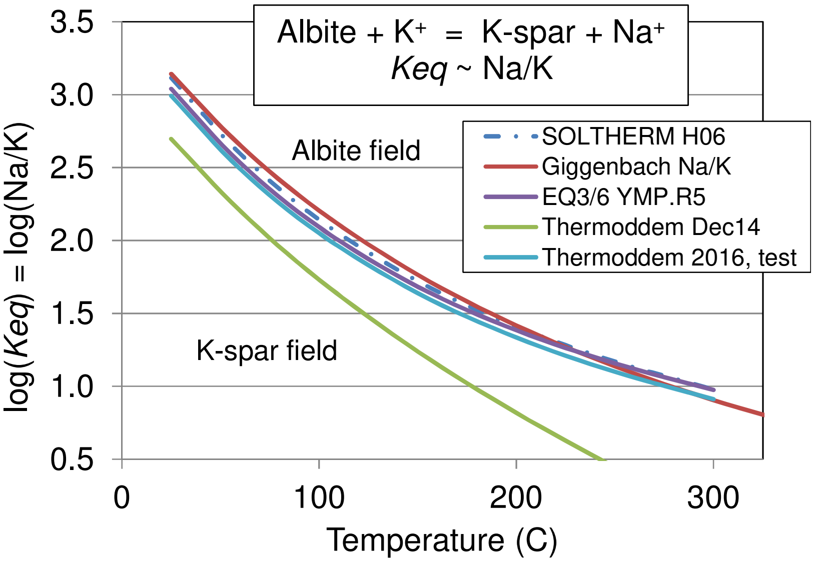

Figure 3 - Na/K geothermometer depending on temperature.

The Taupo Volcanic Zone of New Zealand harbors the Wairakei geothermal system with producing wells reaching temperature > 200°C. This example had been previously used by Bruton (1995) to test the capabilities of the EQ3/6 code and database to predict the temperature of the local geothermal waters, supposing equilibrium with a group of minerals and based on measured concentrations of dissolved elements. The results of the calculation performed by the author are reproduced on figure 4, considering the minerals: wairakite, adularia, epidote, quartz, albite, chlorite, calcite, prehnite and pyrite (Reyes, Giggenbach and Christenson, 1993).

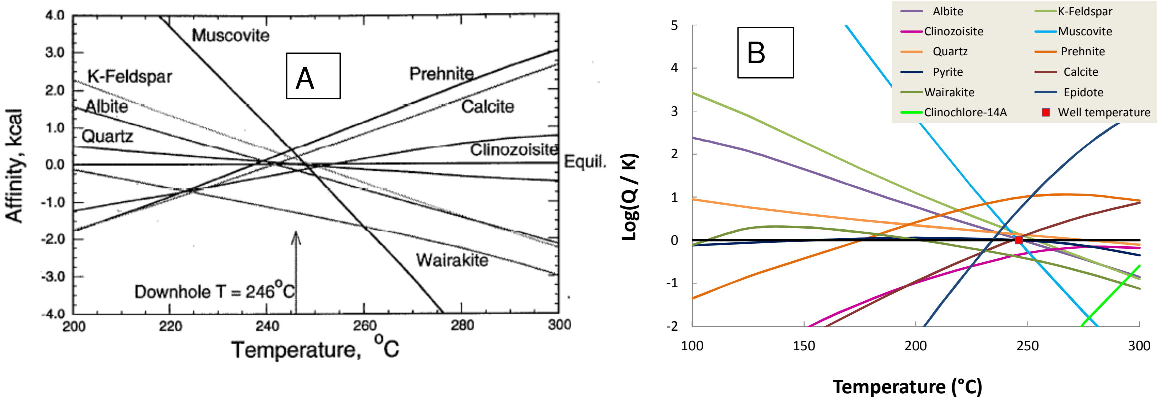

Figure 4 - Affinity calculation, based on Bruton (1995) datasets for the Wairakei site: A – Original Bruton (1995) calculations and B: Calculations using PhreeqC and the EQ3/6 database

In the Bruton (1995) calculations, the curves representing the affinity of the minerals for the dissolution reaction are globally crossing the 0 kcal line close to the well temperature, 246°C. The calculations realized using PhreeqC and the Eq3/6 database display much dispersed results, indicating either problem in the starting hypotheses and/or modifications of the original databases properties in the recent Eq3/6 version (distributed with PhreeqC).

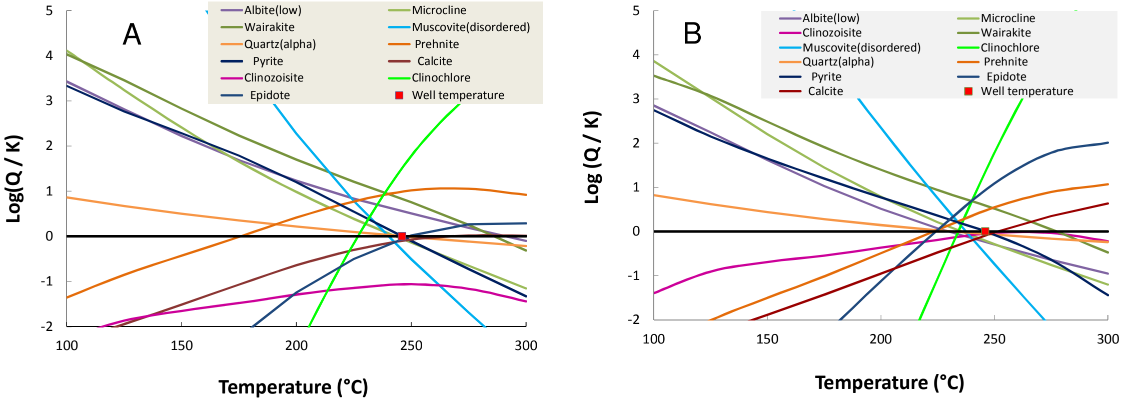

Figure 5 - Affinity calculation, based on Bruton (1995) datasets for the Wairakei site, using the Thermoddem database: A – Using the 2014 released B: Using the proposed modifications

In Figure 5, the calculations are realized using PhreeqC and the Thermoddem database with the 2014 release (Figure 5.A) and including the modification proposed here (Figure 5.B). It appears clearly that the proposed modification does significantly improve the results, with respect to the measured well temperature. Wairakite still remains an issue. Its properties have been adjusted by Bruton (1995). The properties in Thermoddem arise from a selection which considers a whole set of zeolitic minerals (Blanc et al., 2015) and the modifications, if required, would concern 5 different zeolites. Additional data to the present verification exercise would be necessary.

Obviously, the verification exercise has its limits. Only one case is considered, we could not access the original document reporting the analyses of the minerals, which makes it difficult to evaluate the relations between the mineral assemblage and the solution composition reported by Bruton (1995). For example, the composition of the real minerals may not correspond exactly to the theoretical end-members implemented in the database. The water from the production well may undergo mixing …

The estimation approach followed for the aqueous complexes is a matter of debate. A point is that for a given complexation reaction, a very large number of possibilities exists for writing an isocoulombic/isoelectric reaction. The scattering of the resulting values (S° for example) is large and, to our knowledge, there is no guideline to help this choice. Waiting for such guidelines, it remains a questionable issue. An alternative would be to use HKF coefficient estimates, at least for comparison purposes.

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