



Thermodynamic models for solid-liquid equilibrium of aluminum, and aluminum-silicate minerals in natural fluids. Current state and perspectives

Термодинамични модели за твърдо-течно фазово равновесие на алуминиеви и алуминиево-силикатни минерали в природни флуиди. Състояние и перспективи

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Chemical models that predict solution behavior and solid-liquid-gas equilibria close to experimental accuracy over broad ranges of composition, temperature and pressure (XTP) have wide applicability. They can simulate the complex changes that occur in nature and can replicate conditions that are difficult or expensive to duplicate in the laboratory. The application of chemical models permits systematizing numerous literature data on the activities and solubilities in binary, and complex systems and estimating their correctness. The development of these models facilitates very much the study of the corresponding systems and the solution of applied problems. Such models can be powerful predictive and interpretive tools to study the geochemistry of natural waters and mineral deposits, solve environmental problems and optimize industrial processes. Development of comprehensive models for natural and industrial multicomponent systems, with their complexity and sensitivity, is a very difficult, time consuming and challenging task. The systems of interest are mostly highly non-ideal and predicting of their properties is very complicated task, because the thermodynamics of fluids is a sensitive function of their composition, temperature and pressure.

The specific interaction approach for describing electrolyte solutions from low to high concentration introduced by Pitzer (1973, 1991) represents a significant advance in physical chemistry that has facilitated the construction of reliable thermodynamic models. It was showed that this approach could be expanded to accurately calculate activities and solubilities in complex brines and to predict the

behavior of natural fluids in a wide range of concentration and temperature (Moller et al., 2005, 2006, 2007; Christov, Moller, 2004; Christov, 2005, 2009; Christov et al., 2007). The main purpose of research activity described in this study is to develop Pitzer formalism (Pitzer, 1973, 1991) based XTP-variation, well validated thermodynamic database, which accurately describe solution properties and stable (laboratory) and metastable (natural) phase equilibrium of aluminum, and aluminum-silicate minerals in natural fluid systems. Here I summarize our progress in developing a model describing geochemical behaviour of Al (III) and Si (IV) minerals in natural fluid system with a composition H-Na-K-NH₄-Mg-Ca-Cl-OH-SO₄-HSO₄⁻-Al⁺⁺⁺-Al(OH)⁺⁺-Al(OH)₂⁺-Al(OH)₃⁰-Al(OH)₄⁻-H₃SiO₄⁻-H₄SiO₄⁰-H₂O (Table 1). The developed models, are not concentration (X: from 10⁻⁸ to 15 mol.kg⁻¹), and not-temperature (T: from 0° to 250(300) °C) – restricted, and consider all experimentally identified solid phases, which precipitate from saturated and supersaturated solutions. Table 2 summarized Al(III) and Si minerals included into the solution model (Table 1) for geochemical behavior of aluminum (Christov, 2001, 2002a, b, 2003, 2005, 2009; Moller et al., 2005, 2006, 2007; Christov et al., 2007; André et al., 2019).

The resulting comprehensive Al(III) models will be used to describe correctly the geochemical behavior of aluminum in acidified waters and to solve many problems concerning: (1) aluminium hydroxide (gibbsite, boehmite), and aluminium sulphate (alunogen, alums, tamagurites), and aluminium – silicate (kaolinite, dickite, feldspars), and

Table 1. Current status of comprehensive fully parameterized models for multicomponent Al (III) and Si (IV) minerals natural systems

(1) Acid-base H-Na-K-Ca-OH-Cl-SO ₄ -HSO ₄ -H ₂ O model from 0° to 250 °C	Calculates solution activities and solid liquid equilibria of 11 sodium-potassium-acid-base solid phases, 3 calcium base, and 3 calcium chloride minerals	Christov, Moller (2004)
(2) Silica model (from 0° to 250 °C)	H ₄ SiO ₄ ⁰ -H ₃ SiO ₃ ⁻ interactions added to model (1). Calculates solution activities and solid liquid equilibria of 5 pure silica (SiO ₂ (cr)) and SiO ₂ ·2H ₂ O(cr) minerals	Moller et al. (2007)
(3) Ideal Solution-Polynuclear (PN) aluminum species model	solution model that estimate the impact of Al ₂ (OH) ₂ ⁴⁺ , Al ₃ (OH) ₄ ⁵⁺ , Al ₁₃ O ₄ (OH) ₂₄ ⁷⁺ and Al ₁₃ O ₄ (OH) ₂₄ (H ₂ O) ₁₂ ⁷⁺ PN species on the total Al concentration in natural waters at 25° and 100 °C	Moller et al. (2005)
(4) H-Na-K-Mg-Al-Cl-H ₂ O model from 0° to 125 °C	calculates solution activities and solid liquid equilibria of gibbsite and boehmite in acid aluminum solutions	Christov et al. (2007), Christov (2009)
(5) Model for H-Na-K-Al-Cl-OH-Al(OH) ⁺⁺ -Al(OH) ₂ ⁺ -Al(OH) ₃ ⁰ -Al(OH) ₄ ⁻ -H ₂ O system (0° to 250 °C (300 °C))	calculates mononuclear Al(III) hydrolysis solution speciation activities, and gibbsite & boehmite and Al-Si minerals precipitation in pH range from 2 to 10. Many binary and mixing Al parameters are added to model (1)	Moller et al. (2006, 2007)
(6) Al-Cr model for stable and metastable equilibrium in Na-K-NH ₄ -Mg-Al-Cr-Cl-SO ₄ -H ₂ O system at 25 °C	new Cr(III) and Al(III) chloride and sulfate binary and mixing parameters and stable and metastable solid liquid equilibria of 12 Al, and Al-Cr solids are introduced into a solution model	Christov (2001, 2002 a, b, 2003, 2005)
(7) A model for solution behavior and solid-liquid equilibrium in Na-K-Mg-Ca-Al(III)-Fe(III)-Cr(III)-Cl-H ₂ O system at 25 °C	new Al(III) mixing parameters are added to models (1), (4) and (5)	André et al. (2019)

Table 2. Al(III) and Si solid phases to be included into the solution models (from 1 to 7) in Table 1

Mineral	Composition	Mineral	Composition
<i>Simple Al(III) minerals</i>		<i>Pure Si(IV) minerals</i>	
Aluminum chloride	AlCl ₃ ·6H ₂ O(s)	Quartz	SiO ₂ (s)
Gibbsite	Al(OH) ₃ (s)	Chalcedony	SiO ₂ (s)
Boehmite	AlOOH(s)	Cristobalite	SiO ₂ (s)
Alunogen	Al ₂ (SO ₄) ₃ ·nH ₂ O (n=16,17,18)	Amorph. silica	SiO ₂ (s)
<i>Double Al-SO₄ salts</i>		Amorph. silica	SiO ₂ ·2H ₂ O(s)
Sodium-alum	Na ₂ (SO ₄)·Al ₂ (SO ₄) ₃ ·24H ₂ O	<i>Al(III)-Si(IV) minerals</i>	
Sodium-tamagurite	Na ₂ (SO ₄)·Al ₂ (SO ₄) ₃ ·12H ₂ O	Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄ (s)
Potassium alum	K ₂ (SO ₄)·Al ₂ (SO ₄) ₃ ·24H ₂ O	Dickite	Al ₂ Si ₂ O ₅ (OH) ₄ (s)
Pot. tamagurite	K ₂ (SO ₄)·Al ₂ (SO ₄) ₃ ·12H ₂ O	<i>Na(I)-Al(III)-Si(IV) minerals</i>	
Ammonium alum	(NH ₄) ₂ (SO ₄)·Al ₂ (SO ₄) ₃ ·24H ₂ O	Low albite	NaAlSi ₃ O ₈ (s)
Ammonium tamagurite	(NH ₄) ₂ (SO ₄)·Al ₂ (SO ₄) ₃ ·12H ₂ O	High albite	NaAlSi ₃ O ₈ (s)
Mg-Al sulfate	Mg(SO ₄)·Al ₂ (SO ₄) ₃ ·22H ₂ O	<i>K(I)-Al(III)-Si(IV) minerals</i>	
<i>Basic Aluminum Sulfate (BAS) minerals</i>		Microcline	KAlSi ₃ O ₈ (s)
Jurbanite	Al(SO ₄)(OH)·5H ₂ O	Sanidine	KAlSi ₃ O ₈ (s)
Basaluminite	Al ₄ (SO ₄)(OH) ₁₀ ·5H ₂ O		
Alunite	KAl ₃ (OH) ₆ (SO ₄) ₂		
Natroalunite	NaAl ₃ (OH) ₆ (SO ₄) ₂		
BAS	k Al ₂ O ₃ ·l SO ₃ ·m H ₂ O (k= 1, 2, 5 l=1, 2, 6; m=6, 9, 12, 46)		

basic aluminium – sulphate (alunite, natroalunite, basaluminite, jurbanite) should be considered in natural waters equilibrium, i.e. what is the standard state of natural equilibrium?; (2) what is the distri-

bution of aqueous aluminum hydroxide(Al(OH)⁺⁺-Al(OH)₂⁺-Al(OH)₃⁰-Al(OH)₄⁻), and aluminium sulfate (AlSO₄⁺, Al(SO₄)₂⁻) species in solutions in equilibrium with each aluminium minerals?; (3) what are

the saturation conditions of natural waters with respect to any relevant aluminium minerals?; (4) what are the pH ranges, total aluminum, chloride, sulphate and silicate concentrations in stability zones of precipitation of minerals?; (5) what is the effect of minerals phase transition on the pH of equilibrium natural solutions?; (6) what is the buffering effect (increasing pH of acid waters) of minerals' crystallization? The resulting Al (III) model can be used to understand more precisely the mechanism of acidification and alkalization of fresh waters through water rock interactions and to predict chemical reaction scheme of corrosion of aluminum in contact with deliquesced sea-aerosols, and in aggressive acidic atmosphere. The resulting extremely comprehensive model described in Table 1 and 2 can be also used to predict the behavior of Al (III) and Si (IV) minerals in nuclear waste and carbon dioxide storage.

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