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## **Development of a Mineral-Specific Sorption Database for Surface Complexation Modeling**

## **Entwicklung einer mineralspezifischen Sorptions-Datenbank für Oberflächenkomplexierungsmodelle**

Förderprojekt PtWt+E 02E9471

Part I: Final Report  
Part II: Manual



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Dresden, September 2004



## Abstract

An MS Access based digital thermodynamic sorption database has been developed and tested. This database is named "RES<sup>3</sup>T - Rossendorf Expert System for Surface and Sorption Thermodynamics". It is mineral-specific and based on the concept of surface complexation (Surface Complexation Modeling – SCM). This concept is able to substitute distribution coefficients ( $K_d$  values) and to improve considerably the characterization of sorption processes. Accuracy and reliability of contaminant transport prognosis are increased thereby.

An integrated user interface helps to access selected mineral and sorption data, to extract internally consistent data sets for sorption modeling, and to export them in formats suitable for other modeling software. Data records comprise mineral properties, specific surface area values, surface binding sites characteristics, sorption ligand information, and surface complexation reactions.

The content of the database is very diverse and comprehensive. Based on 1460 literature references, data records for 111 minerals, 879 sample specific data, 1047 protolysis data records and 2611 surface complexation constants are stored inside RES<sup>3</sup>T (as of July 31, 2004).

The elements covered by RES<sup>3</sup>T comprises the actinides and fission products as well as the heavy metals and As, but also major constituents of the background media (groundwater, seepage water, solutions from corrosion processes).

## Zusammenfassung

Es wurde eine unter MS Access implementierte digitale thermodynamische Sorptionsdatenbank entwickelt und getestet. Die Datenbank mit dem Namen "RES<sup>3</sup>T - Rossendorf Expert System for Surface and Sorption Thermodynamics" - ist mineral-spezifisch und basiert auf dem Konzept der Oberflächenkomplexierung (Surface Complexation Modeling - SCM). Dieses Konzept kann Verteilungskoeffizienten ( $K_d$ -Werte) ersetzen und die Beschreibung von Sorptionsprozessen wesentlich verbessern. Genauigkeit und Verlässlichkeit von Prognosen zur Schadstoffausbreitung werden dadurch erhöht.

Eine integrierte Nutzer-Schnittstelle unterstützt den Zugriff auf ausgewählte Mineral- und Sorptionsdaten, die Auswahl konsistenter Datensätze für die Modellierung der Sorption und den Export in für andere Modellierungssoftware geeignete Formate. Die Datensätze umfassen Informationen zu Mineraleigenschaften, spezifische Oberfläche, Oberflächenbindungsstellen, sorbierenden Liganden sowie Oberflächenkomplexierungsreaktionen.

Der Inhalt der Datenbank ist sehr breitgefächert und umfassend. Basierend auf 1460 Literaturreferenzen sind Datensätze für 111 Minerale, 879 probenspezifische Daten, 1047 Protolysedaten und 2611 Oberflächenkomplexierungskonstanten in RES<sup>3</sup>T erfasst.

Die in RES<sup>3</sup>T enthaltenen Elemente umfassen sowohl Actiniden und Spaltprodukte als auch Schwermetalle und Arsen sowie die Hauptbestandteile der Hintergrundmedien (Grundwasser, Sickerwasser, Lösungen aus Korrosionsprozessen).

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# 1 Introduction

## 1.1 Problem

World-wide activities focus on the remediation of radioactively contaminated sites. One common aim is to deliver a more profound chemical base for risk assessment, namely all those physico-chemical phenomena governing the contamination plume development in time and space. Coupled transport codes able to tackle this challenge have to simplify the resulting very complex reaction pattern. To do so in an adequate way requires to extend the knowledge about retardation and mobilization phenomena and the underlying basic processes and interactions, such as physisorption, chemisorption, coprecipitation, inclusion, diffusion, surface-precipitation, or the formation of solid solutions.

So far, the physico-chemical processes are considered (if at all) by applying conditional distribution coefficients ( $K_d$ ) in order to model the partition of a contaminant between solid and aqueous phases. The  $K_d$  is defined as the experimentally determined ratio of the sorbed (fixed, immobilized) and non-sorbed (free, truly dissolved) fraction of a component (chemical element) under equilibrium conditions. The subsuming of many physico-chemical processes into one purely phenomenological parameter is a severe weakness of the  $K_d$  principle. Such distribution coefficients tend to have large uncertainties especially when inter- or extrapolation to other system conditions is required. They do neglect the underlying chemical reaction mechanisms between solids and the aqueous phase and thus can not reflect changes in chemical environment. Moreover, it is extremely time-consuming to determine  $K_d$  values for the multidimensional parameter space usually to be considered in long-term risk assessment predictions.

To overcome these problems, strategies are required to “unfold” the  $K_d$  approach into more fundamental processes. Such an approach will transform the single distribution coefficient into a vector of parameters, such as  $E_h$ , pH, concentrations of various components, binding site densities, surface areas, and temperature. The unfolding of  $K_d$  values leads to modern concepts that treat surface reactions as complex formations analogous to such reactions in homogeneous aqueous solutions. Therefore these models are called Surface Complexation Models (SCM). SCM are site independent, account for large variations in geochemical conditions and the acquisition of parameters is comparatively cheap. This should make it possible to perform more detailed sensitivity analysis, to find the critical parameters, to reduce the parameter space and, finally, to pave the way for more reliable models for contaminant transport.

## 1.2 Need for Sorption Database

SCM have a high potential to increase confidence in performance assessment (PA) studies:

- They can partially replace  $K_d$  in simple systems.
- It is possible to verify and check measured  $K_d$  values.
- The most sensitive experimental parameters can be identified.
- It is possible to assign uncertainty limits.
- Gaps difficult to access in sorption experiments can be filled by computed values.
- SCM helps to gain a better process understanding.

Furthermore, the SCM concept combined with a powerful sorption database allows a straightforward extension towards rocks and soils composed of several minerals. Their sorption behavior should be predictable from the weighted superposition of the sorption processes for all constituting minerals. This has already been successfully demonstrated by, e.g., Gibb and Koopal (1990), Davis *et al.* (1998) or Arnold *et al.* (2001). The number of really important minerals is limited, since about 20 minerals and mineral groups form more than 95 % of the known rocks forming the earth's crust (Ronov and Yaroshevsky, 1967). Thus the sorption database will be of great benefit for the modeling of complex solids, considerably expanding the application field of thermodynamic sorption models.

To support the above approach a digital thermodynamic database for surface complexation equilibria is essential. Unfortunately, at present there is no such database available world-wide, only  $K_d$  compilations like, e.g., in Ticknor and Rügger (1989) or Petschel *et al.* (1995). Though the US EPA report of Wilhelm and Beam (1999) contains in addition to  $K_d$  values some SCM parameters, the selection of data is restricted and there are no possibilities for user interaction and coupling to speciation software in the printed form. Recently, there has been published a digitized version of a sorption database by Brassler *et al.* (2002), focusing on distribution coefficients for chemical-toxic contaminants and soils.

The lack of a thermodynamic sorption database has various consequences:

- A systematic identification and closing of data gaps becomes very difficult.
- A critical data survey rarely takes place. Hence recommended value sets, as necessary for comparisons of different sorption experiments and sorption modeling, do not exist.

- the compilation of problem oriented data sets from the primary literature needs large effort. Thus they may be incomplete, whereas the selection criteria are often hard to understand by third parties.
- Occasionally, even the use of inconsistent data sets for sorption models can be observed, e.g., the utilization of data of amorphous glass for the description of quartz, or the mixture of data based on different SCM concepts.
- Sorption and, based on this, migration modeling results can therefore exhibit large uncertainties or plain errors, whereby the acceptance of the intrinsically progressive SCM concept is lessened.

Thus it is a logical conclusion that the creation of such a thermodynamic sorption database is an urgent need, being easy to use and comprehensive.

### **1.3 Goals**

The major goal of the project is the design and implementation of a digitized version of a thermodynamic sorption database. It should provide a sound foundation for the use of SCM in risk assessment studies and finally be able to deliver recommended data sets for such SCM applications.

The utilization of thermodynamically consistent data sets is indispensable for a correct modeling of surface complexation. This means that the data sets for the sorption of all relevant ligands on a mineral must be based on identical fundamentals:

- Use the same specific surface area
- Assume the same type and number of binding sites
- Use the same thermodynamic model (SCM)
- Use the same protolysis constants
- Use the same capacities if required by the SCM

Strictly speaking, further qualifications must be fulfilled:

- Same speciation in aqueous solution for all sorption constants;
- Known ionic strength and possibility to extrapolate or interpolate to the model ionic strength

The above mentioned demands on data consistency are realizable only in rare ideal cases. To allow for an at least partial data consistency during the compilation of data sets for special modeling problems, internal references of the underlying specific surface areas, binding sites and protolysis constants must be provided for all surface

complexation constants. These demands are also guidelines for the structure, implementation and utilization of the database (for details see chapter 3).

The result of the project is the **RES<sup>3</sup>T** database, the **R**ossendorf **E**xpert **S**ystem for **S**urface and **S**orption **T**hermodynamics”.

## **1.4 Users and Cooperation**

The announced users comprise

- Scientific community with expertise on contaminant transport and waste management;
- Engineering companies and consultants;
- Risk assessment experts;
- Nuclear and chemical industry;
- Governmental authorities;

which are dealing with problems in

- Storage and disposal of chemically toxic and radioactive wastes;
- Planning and maintaining of municipal waste disposals;
- Closure and remediation of mining influenced areas (brown coal, uranium ore, copper schist, phosphates etc.);
- Safety measures, monitoring and restoration of contaminated military bases and abandoned industrial facilities, or
- Prevention and emergency management of accident scenarios with release of contaminants.

For a successful migration of the RES<sup>3</sup>T database to the announced users a maximum operator convenience is a must. Therefore a straightforward, unrestricted access to the database is coupled with a user-friendly interface.

Over the entire term of the project there was a close cooperation with potential users. Interested people and institutions got a preliminary version of the database (e.g., GRS Braunschweig, PSI Villigen, FZ Karlsruhe), so user interests could be considered through direct feedback from the very beginning.

To further promote RES<sup>3</sup>T, the database (concept, realization and application) was introduced at various national and international conferences. Though then the database was still in a preliminary stage the response by potential users was nevertheless very encouraging.

## 2 Models for the Description of Sorption Phenomena

### 2.1 Fundamentals

There are many attempts in the literature to describe the interactions between ions in solution and a mineral surface in contact with them. These interactions can be grouped into various phenomena, such as physisorption, chemisorption, co-precipitation, inclusion, diffusion, surface-precipitation, or even formation of solid solutions. Surface complexation in a strict sense only describes the chemisorption and has, therefore, to be combined with models for the other effects to ensure a proper thermodynamically based speciation model for the elements of interest. Nevertheless, on shorter time scales it is often the dominating process, having a fast kinetics. Processes such as diffusion of sorbed ions into the host mineral and the subsequent formation of mixed crystals or solid solutions may then follow, but they require much more time. This chapter briefly explains the models most often applied in sorption chemistry. Much more detailed information can be obtained from various textbooks (Dzombak and Morel, 1990; Stumm, 1992; Sposito, 1984) and publications (Davies *et al.*, 1978; Davies and Leckie, 1978; Sposito, 1983; Sposito, 1989; Davies and Kent, 1990; Goldberg, 1995).

Whereas the simplest (and older) sorption models do not distinguish between the various processes outlined above that contribute to the overall sorption, newer model approaches at least describe separately the effects of the electrostatic attraction between a surface and an ion having charges of opposite sign, and the effects coming from a chemical reaction of an ion with a reactive surface site. Therefore, the sorption models are usually grouped into altogether three classes, the phenomenological models and the surface complexation models, with the latter comprising of electrostatic and non-electrostatic models.

For all the formulae the following conventions apply: Brackets, [ ], specify concentrations in mol / L, braces, { }, specify free activities in mol / L. M stands for a metal species (pure cation, hydrolytic or complex species) that can sorb onto a surface, »XOH denotes the protonated, unreacted sorption site. The activity coefficient (dimension depends on reaction equation) of a species *i* is given by  $\gamma_i$ .

## 2.2 Phenomenological Models

### 2.2.1 Distribution Coefficient ( $K_d$ ) Model

The partitioning of dissolved ions between the solution and all relevant surfaces is generally characterized by the equilibrium distribution coefficient  $K_d$ . The  $K_d$  concept is the one most often applied in geochemistry at present. It is used in two different versions, based on either of the following definitions:

a) Conventional  $K_d$  model:

$$(1) \quad K_d = \frac{[\gg XOH - M]}{[M]_T}$$

Here  $K_d$  represents the ratio of the specific concentration of the metal sorbed onto the surface (given in mol/g solid) to the concentration of the dissolved metal (sum over all aqueous species containing the metal, given in mol/L solution).

b) Activity  $K_d$  model:

$$(2) \quad K_d^{act} = \frac{\{\gg XOH - M\}}{\{M\}}$$

Contrary to the above definition, here the activity of the sorbed species and the free metal cation in solution is considered.

### 2.2.2 Langmuir Adsorption Model

The Langmuir adsorption (Langmuir, 1916) differs from the  $K_d$  approach only in that it requires specification of the total number of surface sites available. It assumes a reaction between a distinct surface site and the free metal cation, giving an equilibrium constant according to the equation:

$$(3) \quad K_L^{act} = \frac{\{\gg XOH - M\}}{\{M\}\{\gg XOH\}}$$

This formulation is equal to the expression most often given as:

$$(4) \quad [\gg XOH - M] = K_L^{act} \cdot \frac{[\gg XOH]_T \gamma_M [M]}{1 + K_L^{act} \gamma_M [M]}$$

Whether a description with the Langmuir isotherm is correct can easily be verified by plotting  $[M] / [\gg XOH - M]$ , using a linearized version of the defining equation:

$$(5) \quad \frac{[M]}{[\gg XOH - M]} = \frac{1}{K_L [\gg XOH]_T \gamma_M} + \frac{[M]}{[\gg XOH]_T}$$

The introduction of total surface site densities certainly improves the sorption isotherm concept, because this takes into consideration saturation effects due to the limited number of reactive surface sites that are really accessible in a reaction. This surface site density, however, is a parameter not so easily to determine. It can be obtained from measurements of maximum sorption values (maximum proton uptake), by tritium exchange methods, or through theoretical considerations, for details see Dzombak and Morel (1990). Values determined for the same surface may differ by a factor of two to three. The surface site density is often given the symbol  $\Gamma$  with the units mol/m<sup>2</sup> or sites/nm<sup>2</sup>, but also mol/L solution, mol/mol metal or mol/g solids are reported; so care must be taken when using such values.

### 2.2.3 Freundlich Adsorption Model

The Freundlich model (Freundlich, 1906) again is very similar to the  $K_d$  approach, assuming infinite numbers of surface sites. The difference is that the reacting species  $M$  is assigned a mass action stoichiometric coefficient of  $1/n$ :

$$(6) \quad K_F^{act} = \frac{\{\gg XOH - M\}}{\{M^{1/n}\}\{\gg XOH\}}$$

The applicability of the model can also be checked through a linearized version of the above equation:

$$(7) \quad \log[\gg XOH - M] = \log K_F + \frac{1}{n} \log[M]$$

Other isotherms in use to a lesser amount are named after Toth, Dubinin-Radushkevich, and Frumkin.

### 2.2.4 Ion Exchange Model

This model (Bolt, 1979; Dzombak and Hudson, 1995) describes the process of exchanging an ion from the solution with an ion on the surface of a mineral. Such an ion also can be the proton  $H^+$ . The reaction parameter  $K_{ex}$  actually measures the competition between two ions  $M_A$  (initially occupying the site) and  $M_B$  (replacing ion) for a surface site, therefore  $K_{ex}$  is also called selectivity coefficient:

$$(8) \quad K_{ex} = \frac{\{M_A\} \{\gg XOH - M_B\}}{\{M_B\} \{\gg XOH - M_A\}}$$

## 2.3 Surface Complexation Models (SCM)

### 2.3.1 Basic Principles

To enable a thermodynamic consistent treatment of sorption requires the decomposition of the overall phenomenon into the main basic processes defining it. Such an approach will unfold the single distribution coefficient into a vector of parameters, such as  $E_H$ , pH, concentrations of the various components, binding site densities, surface areas, and temperature.

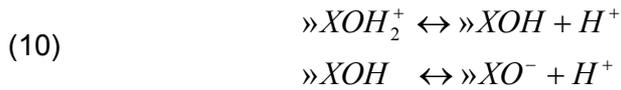
Apparently this is a step backwards, introducing a high degree of complexity and significantly increasing the number of parameters. But it has the great advantage that all these parameters can be measured with more reliability and precision. Knowing the functional relationships between these processes and how they contribute to the  $K_d$  allows a computation of latter rather than a measurement. Moreover, simulations with variable parameter values, even for hypothetical conditions, may easily yield a  $K_d$  surface as a function of the "primary" parameter vector:  $K_d = f(E_H, \text{pH}, p_{\text{CO}_2}, T, \dots)$ . Usually, the function  $f$  can not be expressed as an explicit function but contains implicit formulations only accessible through numeric iterations. Also, some long-term effects that may render conventional distribution coefficients meaningless (co-precipitation, diffusion of trace elements into crystal lattices) can be accounted for in a better way. Another application is expressing  $K_D$  as a function of time, related to better-defined time dependencies of other basic parameters. Furthermore, it becomes possible to identify those parameters affecting the  $K_d$  strongest. Consequently, extra measurements can be designed efficiently to reduce its uncertainty. And last but not least the formal keeping of the used  $K_d$  paradigm renders it easy to couple a "smart  $K_d$ " framework with already existing contaminant transport and risk assessment codes, enhancing its acceptance.

The unfolding of  $K_d$  values leads to the already mentioned Surface Complexation Models (SCM). This requires the definition of surface sites with a finite concentration. Usually such surface sites are represented as  $\gg\text{XOH}$  groups with X denoting a metal from the solid structure, located at the solid-liquid interface. Many mineral surfaces, but especially colloids carry a significant surface charge, creating an electrostatic potential

extending into the aqueous solution. Depending of the charge of the ions they are either attracted or repelled, thus greatly influencing the sorption behavior of charged species (and due to dipolar effects even neutral species). To account in a proper way for this charge effect, additional terms have been introduced into adsorption models, modifying the activity of sorbate ions. These terms describe the electrical work necessary to penetrate the zone of electrostatic potentials, resulting in a difference between the activity of ions  $M_s$  with the charge  $z+$  near the surface and the same ions  $M$  in the bulk solution:

$$(9) \quad \{M_s^{z+}\} = \{M^{z+}\} [e^{-\Psi F/RT}]^{z+}$$

where the second term of the right side, the Boltzmann factor, is defined by the Faraday constant  $F$ , the ideal gas constant  $R$ , the absolute temperature  $T$ , and the electric potential  $\Psi$  near the surface. The activity of surface species is set to one by definition. Another essential assumption is the diprotic acid model used to describe the protonation and deprotonation of surface sites (2-pK approach):



During some surface complexation experiments it turned out, that the observations could only be explained satisfactory when assuming two site categories on one surface, having different binding properties: "strong" and "weak" binding sites with differing surface site densities. The strong binding surface sites are considered to be acidic, with a large degree of polarization. Weak binding sites are basic sites, with a much lesser degree of polarization, very similar to anion exchange sites. This concept is applied mostly to cation sorption, for anions no significant difference in sorbing on strong and weak sites could be detected. So identical complex stability constants are used (which reduces the number of parameters somewhat) for both site types. Fortunately, when dealing for sorption of contaminants in natural systems, the concentration of contaminants is near to trace levels. However, in cases, where the concentration of the sorbing ions is considerably larger, surface precipitation may become important. It is worthwhile to note, that such precipitations onto a surface will already occur at concentrations below the values that must be exceeded in the bulk solution, because the solid activity on surfaces is less than unity.

### 2.3.2 Constant Capacitance Model

The Constant Capacitance Model (Schindler and Gamsjäger, 1972; Hohl and Stumm, 1976) assumes only one layer or plane (o-plane) between surface and bulk solution. All specifically adsorbed ions contribute to the surface charge in this layer. The total charge  $\sigma$  is computed using a constant capacitance term  $C$  according to:

$$(11) \quad \sigma_o = C \Psi_o$$

Actually, the constant capacitance model is just a special case of the diffuse layer model for solutions of high ionic strength ( $I > 0.01$  mol/L) and surfaces of low potential, see especially Hayes *et al.* (1991). It is strongly dependent from the ionic strength, and requires one more parameter than the Diffuse Double Layer model. The positioning of ions and the correlation between charge and potential is shown in Fig. 1:

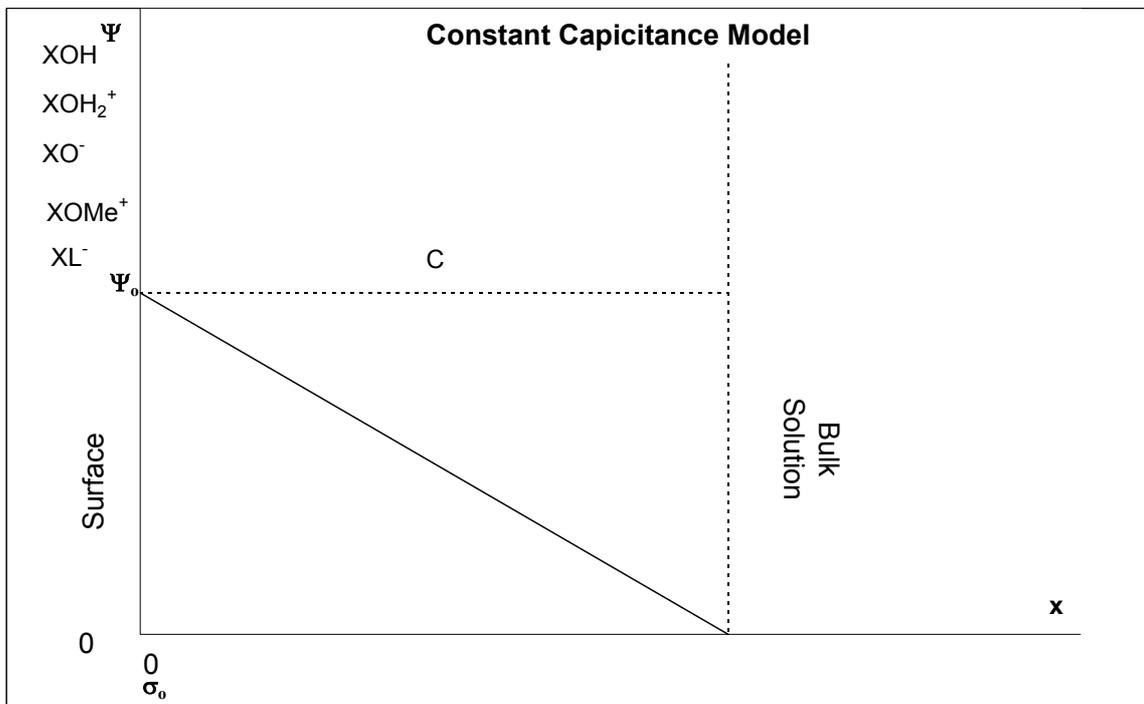


Fig. 1: Positioning of ions and correlation between charge and potential for the Constant Capacitance Model

### 2.3.3 Diffuse Double Layer Model

In the Diffuse Double Layer Model (Stumm *et al.*, 1970; Dzombak and Morel, 1990) the total charge  $\sigma$  is defined by the following equation, with all parameters being defined already before:

$$(12) \quad \sigma_o + \sigma_d = 0 \quad \text{with} \quad \sigma_o = 0.1174\sqrt{I} \sinh\left(Z \Psi_o \frac{F}{2RT}\right)$$

An important advantage of this rather simple approach is, that there are no electrostatic parameters required at all. This reduces data needs and consequently data uncertainty, for a detailed discussion see Dzombak and Morel (1990). Ionic strength dependence is taken into account as long as  $I$  is below 0.1 mol/L. However, there are other cases, where this approach can not be applied because of a more complex surface chemistry. The position of ions and the correlation between charge and potential is shown in Fig. 2.

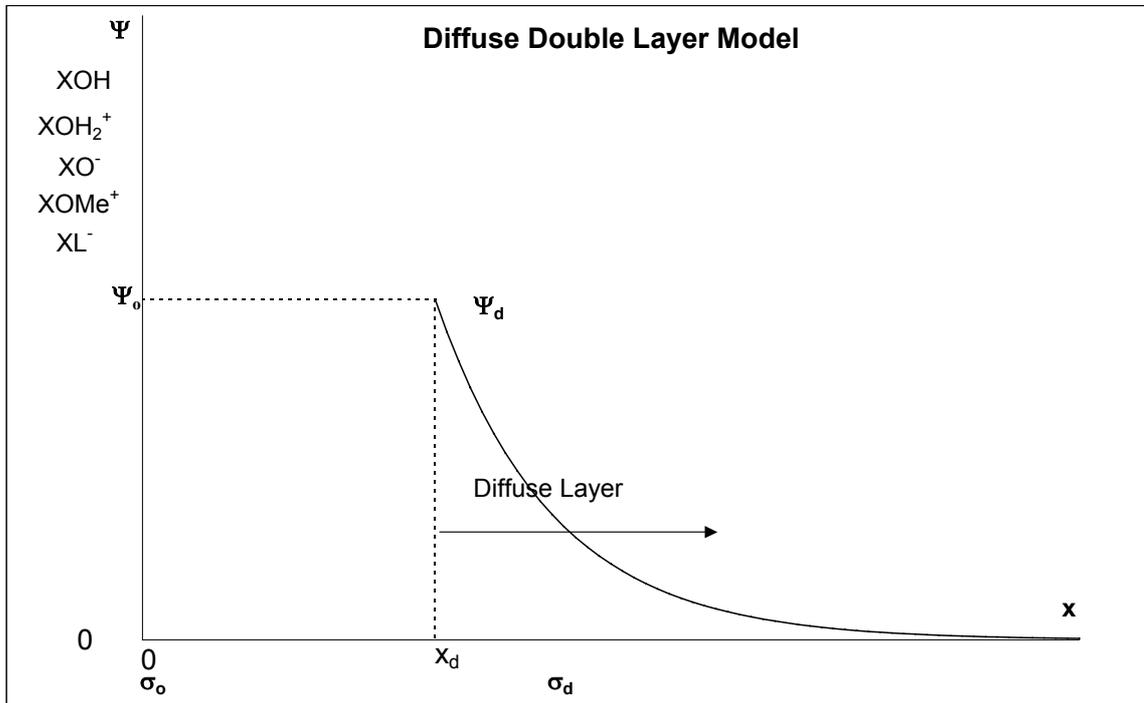


Fig. 2: Positioning of ions and correlation between charge and potential for the Diffuse Double Layer Model

### 2.3.4 Triple Layer Model

In the Triple Layer Model (Yates *et al.*, 1974; Davis *et al.*, 1978) two different planes are assumed for the surface: The innermost or  $\alpha$ -plane does only incorporate protonation or deprotonation of surface sites. All other specifically adsorbed ions are assigned to the outer or  $\beta$ -plane. Therefore, each plane has its own charge and potential. The third layer (to justify the name of the model) is as in the above models the diffuse layer. See Fig. 3 for a schematic picture. The total charge for these three planes are computed from the respective capacitances  $C$  and potentials  $\Psi$ :

$$\begin{aligned}
 (13) \quad & \sigma_o + \sigma_\beta + \sigma_d = 0 \\
 & \sigma_o = C_{o-\beta}(\Psi_o - \Psi_\beta) \\
 & \sigma_\beta = C_{o-\beta}(\Psi_\beta - \Psi_o) + C_{\beta-d}(\Psi_\beta - \Psi_d) \\
 & \sigma_d = C_{\beta-d}(\Psi_d - \Psi_\beta)
 \end{aligned}$$

The charge  $\sigma_d$  of the diffuse layer is for monovalent symmetric electrolytes given by the Gouy-Chapman equation with the dielectric constant  $\varepsilon$  and the permittivity in vacuum  $\varepsilon_0$ :

$$(14) \quad \sigma_o = -\sqrt{\varepsilon \varepsilon_0 RT I} \sinh\left(\Psi_d \frac{F}{2RT}\right)$$

Here we have thus two additional electrostatic parameters,  $C_{o-\beta}$  and  $C_{\beta-d}$ , often just referred as  $C_1$  and  $C_2$ . To reduce the number of variable model parameters,  $C_2$  is often generally fixed to 0.2, whereas  $C_1$  is a fitting parameter inside a range between 0.1 and 2.0, which is supported by theoretical considerations.

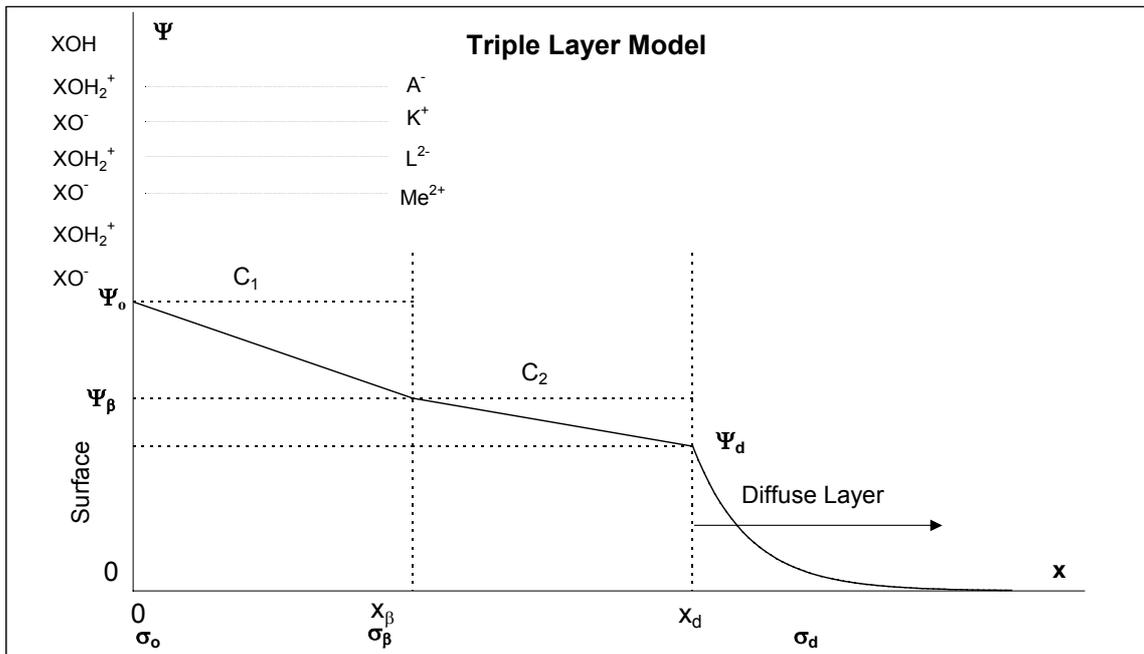


Fig. 3: Positioning of ions and correlation between charge and potential for the Triple Layer Model

### 2.3.5 Other Models

#### Basic Stern Model

The Basic Stern Model (Bowden *et al.*, 1977; Westall and Hohl, 1980) perhaps can be considered as combination of Constant Capacitance and Diffuse Double Layer Model (see Fig. 4), furthermore it considers the sorption of background electrolyte ions. The Basic Stern Model also takes account of the fact that both the surfaces and adsorbing species are charged and that the surfaces change their charge when ionic sorption takes place. The solid-solution interface comprises of an empty Stern layer and a flat diffuse double layer. The correlation between surface charge  $\sigma$  and surface potential  $\psi$  can be described similar to the Triple Layer Model, but with only one capacity:

$$\begin{aligned}
 (15) \quad & \sigma_o + \sigma_\beta + \sigma_d = 0 \\
 & \sigma_o = C_{o-\beta} (\Psi_o - \Psi_\beta) \\
 & \Psi_\beta = \Psi_d
 \end{aligned}$$

The surface functional group is defined by HO-X-OH<sub>2</sub>. This convention allows only one protonation or dissociation to occur for every two surface hydroxyl groups.

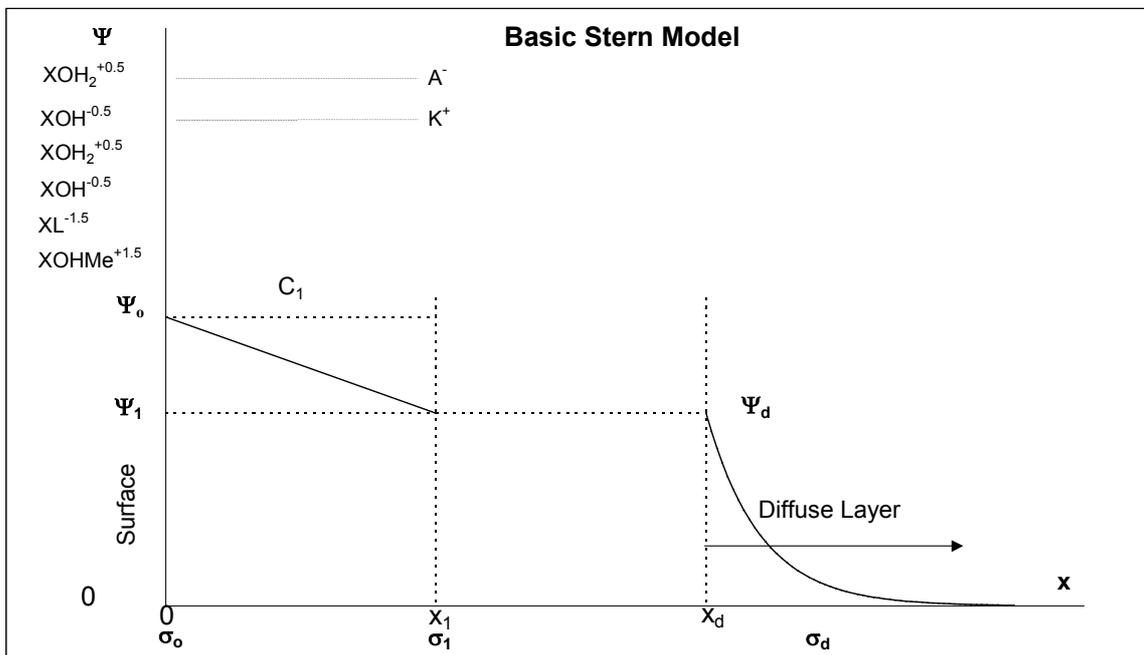


Fig. 4: Positioning of ions and correlation between charge and potential for the Basic Stern Model

### **1-pK-Model**

Other than the generic 2-pK formalism the 1-pK-approach (Bolt and van Riemsdijk, 1982; Hiemstra *et al.*, 1987) describes the charge of the surface by an assumption of only one equation



and replaces so the protolysis equations in chapter 2.3.1. Up to now this approach is not so widely used yet. The Constant Capacitance Model, the Diffuse Double Layer Model and the Triple Layer Model all in principle can be combined with this approach, but the Stern Model and the (CD-)MUSIC Model are the most often utilized combinations with the 1-pK-Model.

### **(CD-)MUSIC Model**

The MUSIC (Multisite Complexation) (Hiemstra *et al.*, 1989) and its extension CD-MUSIC (Charge Distribution Multisite Complexation) Model (Hiemstra and Van Riemsdijk, 1996) have been developed to consider the dissimilitude of surface sites and crystal surfaces. This approach enables a more realistic description of surface species and binding mechanisms than the conventional surface complexation models, but demands a detailed knowledge of morphology and crystal structure of the particle surface (character and distribution of the binding sites). Three differently coordinated surface sites are assumed, which are in the deprotonated state are  $\gg X-O^{-3/2}$ ,  $\gg X_2-O^-$  und  $\gg X_3-O^{-1/2}$ . Therefore only two forms can generate charged sites:  $\gg X-OH^{-1/2}$  und  $\gg X_3O^{-1/2}$ .

### **2.3.6 Non-Electrostatic Surface Complexation Model**

Unlike other SCM, the Non-Electrostatic Model (Kurbatov *et al.*, 1951; Bradbury and Baeyens, 1997) assumes that electrical charge at mineral surfaces does not effect the surface complexation. Thus, the activity of a surface species is equal to its concentration. An apparent equilibrium constant is calculated.

Although this model oversimplifies surface complexation, several investigators have used this approach to describe sorption. One of the reasons may be that the Non-Electrostatic Model requires the fewest fitting parameters.

The description of acid-base equilibria of pure oxidic surfaces is insufficient when using a Non-Electrostatic Model, whereas equilibria of clays can be described more success-

fully. Davis *et al.* (1998) argued that this model may be the most appropriate model for complex environmental applications because the surface charging behavior of non-ideal nature mineral phases is not well known.

## **3 Design of the Database**

### ***3.1 Structural Design & Implementation***

The database is designed as a Relational Data Base System (RDBS). All information is structured into logical subunits, stored into separate tables which are logically connected by the RDBS. This ensures that every piece of information is only stored once. Other benefits are high efficiency and internal consistency. In Fig. 5, a sketch of the major tables, their data elements, and their mutual relationships is given. The modular design also eases later extensions, such as inclusions of surface complexes with organics (e.g. humic acids), or interactions between surfaces and living matter (e.g. microbes).

The database is implemented in Microsoft Access on PC, providing an integrated graphical development system together with the RDBS. Data records can be displayed as tables, in forms or reports. Possible data types are: numeric, logic, text, binary object. Queries to the database can be performed with the standardized Structured Query Language (SQL), opening the opportunity to access external, additional databases, e.g., about rocks and soils, or with crystallographic information. The programming of the database functionality has been enhanced by means of the Visual Basic for Application (VBA) programming language.

### ***3.2 Information Coverage***

The database covers all the main surface complexation models in use at present, discriminating from each other by the way they handle electrostatic contributions to the Gibbs Free Energy of surface complex formation:

- Non-Electrostatic Model (NE)
- Diffuse Double Layer Model (DDL)
- Constant Capacitance Model (CC)
- Triple Layer Model (TL)
- Basic Stern Model (BS)
- 1-pK approach: (Charge Distribution Multisite Complexation Model (CD-MUSIC) and 1-pK Basic Stern (1-pK BS))



Fig. 5: Internal relationships and content of the data tables of RES<sup>3</sup>T

An extension to other models is possible. For every SCM type (where applicable), the concept of strong and weak binding sites after Dzombak and Morel (1990) is included. Surface species composed from up to two different ligands can be incorporated.

In general, all parameters recorded in the database are traced back to the original publication, including as many experimental details as possible to permit an evaluation of the data items. All internal relationships of complex data sets are stored, assuring a maximum of transparency and enabling the selection of internally consistent parameter sets. Internal consistency means, that a complete data set for a mineral surface and several aqueous complexing ligands (ions) is based upon the same values for the surface binding site density, utilizes the same surface complexation model, applies identical site protolysis constants and (if applicable) the same electric capacitance values. It also means that, together with any reaction constant, the original ionic strength and medium must be stored to allow later extrapolations to other desired conditions. In a strict sense, even the pertinent aqueous speciation pattern in equilibrium with the surface complexes at the experimental conditions should be recorded, which is at the moment not implemented yet, however.

The data records contain information about:

- Minerals: English names (official and trivial ones), formula, density, molar mass, reaction paths (aging, weathering, formation of secondary phases) with the appropriate reaction products, chemical equation, and thermodynamic and kinetic constants
- Mineral surface properties (sample specific): specific surface area (with associated grain size fraction), point of zero charge, origin and treatment of the solid
- Surface binding sites: concentration, type (strong / weak affinity, tetrahedral / octahedral coordination etc.), protolysis constants, applied SCM type, capacitance values, ion exchange capacity
- Chemical ligands (aqueous components / ions / master species) which can be both inorganic or organic ones: constituting elements, stoichiometry, charge, radius, redox state, molar mass
- Surface complexes: species, experimental (e.g. spectroscopic) or theory-based evidence, reaction equation, formation constant, chemical structure.

For any value the experimental method used to derive this value is stored, together with the respective ionic strength and background media, as well as any other information necessary to evaluate the data or to calculate other derivative values. If published, uncertainty limits for numerical data are included. This is a prerequisite for sensitivity

and uncertainty analysis. In addition to the “hard” experimental results and parameters, an extensive bibliography is provided too. Every stored data item is linked to both original citations and secondary literature references. The references also comprise model evaluations with respect to theoretical limitations, thermodynamic consistency and parameter sensitivity. Moreover, they cover questions of experimental design and interpretation of results from sorption experiments, or experimental methods used for such investigations with their associated error ranges and application areas. All this means a transition from a pure data collection towards a “smart” database, which ultimately will turn into a sorption expert system. This purpose is supported by the already broad variety of user interactions offered.

### **3.3 User Interaction**

Instead of just being a (printed) collection of sorption data, the computer-based relational database opens additional opportunities of data processing by potential users. The database contains a graphical user interface with two classes of hierarchical forms. The first class serves for data input and editing, the second one enables the selection, viewing, and exporting of specific data sets. To prevent unauthorized data manipulation and the emergence of different unsynchronized database versions, the whole editing shell can be uncoupled and hidden from the user. This is the default case, leaving the following opportunities for user-database interactions:

- Users can easily extract specific data sets, e.g. all records relevant for the combination of a specific mineral and a specific SCM.
- They can also choose to show all sorption data available for a certain element / ligand / ion, or all published surface area data of a mineral.
- Once a data set has been generated, it can be shown on the screen or printed out.
- Data selection can be exported in a file to be used in other geochemical specification codes. Actually, this is possible as Excel spread sheet or ASCII file.
- Original bibliographic references can be traced back. From there other parameter sets stemming from the same source can be viewed.
- Each data record has a time stamp and editing remarks. Therefore it is easy to reconstruct past data set assemblages at any later time, or to check alternative data sets for a sorption modeling scenario.
- The user is supplied with an integrated online help in addition to an exhaustive printed documentation (manual).

### **3.4 Integrated Tools**

The following tools as part of RES<sup>3</sup>T simplify a comparison and uniform processing of the stored data:

- Automatic conversion of surface site densities in one unit (sites/nm<sup>2</sup>).
- Normalization of pK and logK values to a reference surface site density of 12.05 sites/nm<sup>2</sup> (Kulik, 2002).
- Automatic proposal of a chemical reaction equation (for the surface complex formation) after input of the stoichiometric coefficients
- Statistical Data Evaluation:
  - Specific surface distributions referring to minerals.
  - Protolysis data distributions referring to minerals.
  - LogK distributions referring to ligand, SCM models, minerals, and mineral groups.
  - Publication statistics referring to journals and year.
- Reformatting of bibliographic references according to editorial guidelines of different journals.

## 4 Database Content

### 4.1 Publications

About 1400 literature references are already stored in the RES<sup>3</sup>T database. There, the majority of information is published in journals, whereof the Journal of Colloid and Interface Science, Geochimica et Cosmochimica Acta, and Environmental Science and Technology are the main source of SCM data. Fig. 6 shows the relative amount of published SCM papers by the major journals. Other important data source categories are books, reports, conference proceedings, Ph.D. and M.Sc. thesis.

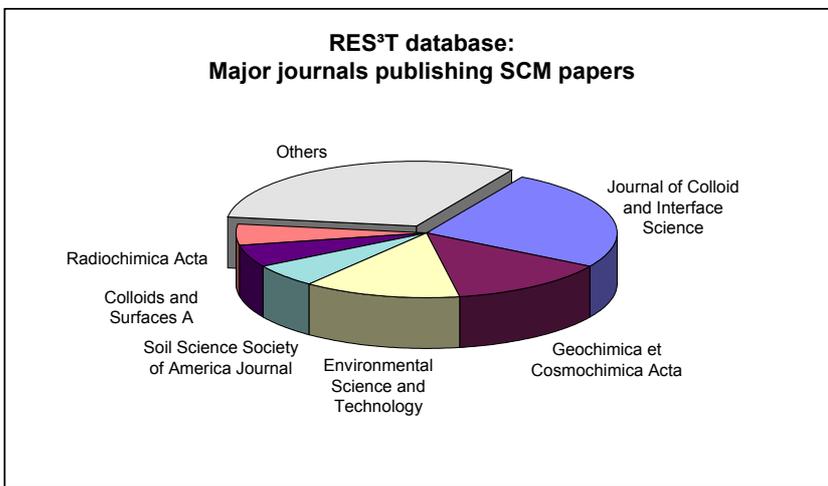


Fig. 6: Major journals publishing SCM papers

### 4.2 Minerals

At present, more than hundred minerals are available in the database. They are categorized into several mineral groups based on the chemistry and structure of the minerals, namely the dominating anion:

feldspars, pyroxene, amphibole, mica, olivine, Fe oxides/hydroxides, Al oxides/hydroxides, Mn oxides/hydroxides, other oxides, clay minerals, other silicates, Ti oxides, carbonates, quartz varieties, phosphates, others.

In parallel, the minerals are also grouped into various series based on petrologic considerations:

rock forming minerals 1:	feldspar, quartz
rock forming minerals 2:	pyroxene, amphibole, mica, olivine
rock forming minerals 3:	others
weathering minerals:	Fe/Al/Mn (hydr)oxides

heavy minerals:  
clay minerals:  
carbonates  
others

oxides (no Fe/Al/Mn), others  
layer silicates (no mica)

### 4.3 Sample Specific Data

The database comprises nearly 900 data sets of sample specific data (sample origin, preparation steps, and analytical results characterizing the samples used in sorption experiments). Fig. 7 shows the distribution of specific surface area data records referring to minerals:

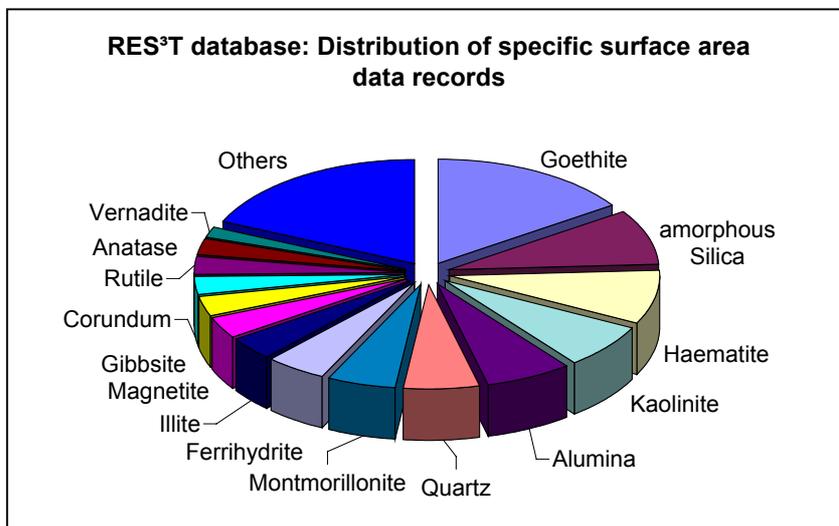


Fig. 7: Distribution of specific surface area data records

### 4.4 Site Density and Surface Protolysis

The distribution of more than thousand protolysis data records with respect to the minerals is shown in Fig. 8. Concerning the solid phases, iron (hydr)oxides, clays, aluminum (hydr)oxides, quartz varieties, and manganese (hydr)oxides are well represented, whereas important rock forming mineral groups such as feldspars, mica, pyroxenes, amphiboles, or olivines have not been investigated to a satisfactory extent.

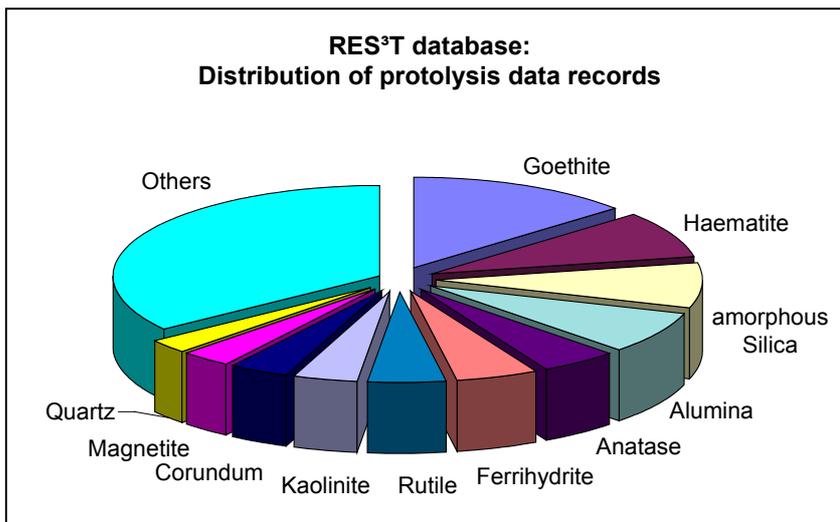


Fig. 8: Distribution of protolysis data records referring to minerals

#### 4.5 Surface Complex Formation

About 2600 data records of surface complex formation constants are gathered in the database. These records are associated to the minerals as shown in the following figure:

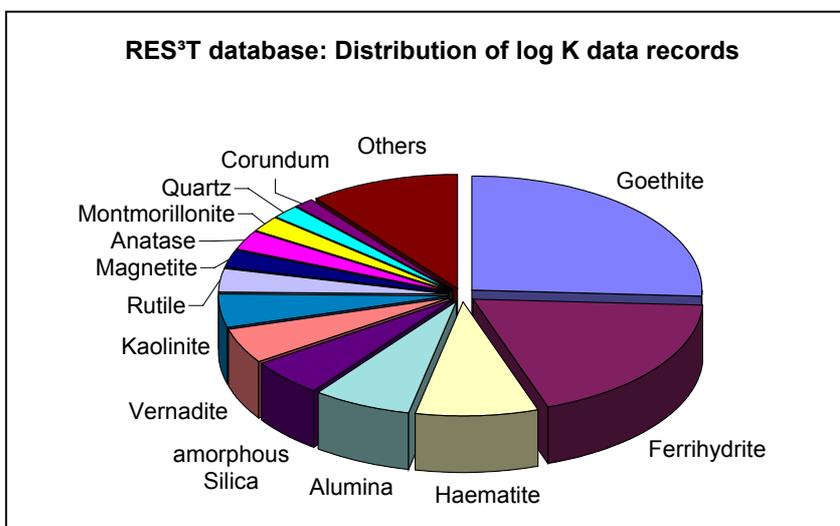


Fig. 9: Distribution of surface complexation constants records referring to minerals

When converting this figure into a distribution with respect to the major mineral groups, the picture looks like in Fig. 10. Obviously most of the sorption experiments so far concentrated on those minerals that are easy to handle in the laboratory and have well-defined surfaces. Whereas some of them have considerable practical relevance others are merely model systems. Especially the important groups of manganese minerals, mica, and feldspars are underrepresented so far.

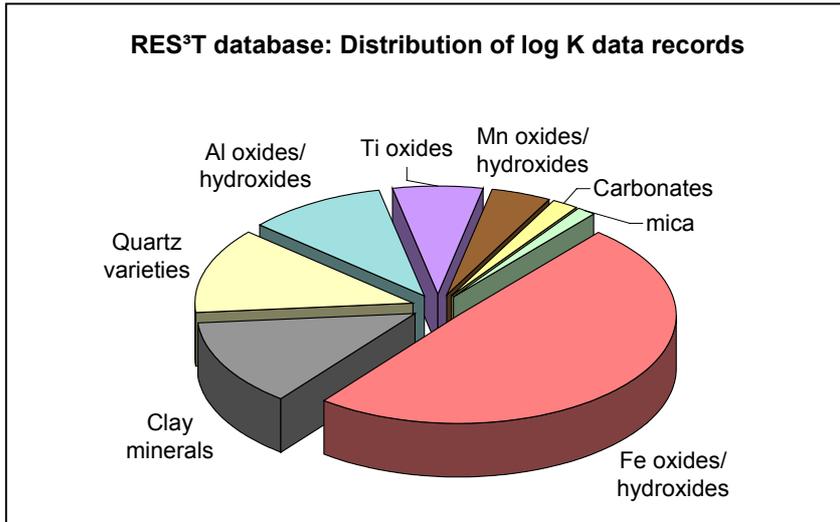


Fig. 10: Distribution of surface complexation constants records referring to mineral groups

In Fig. 11 you can see the distribution of log K data records referring to the major ligands (contaminants and matrix ions).

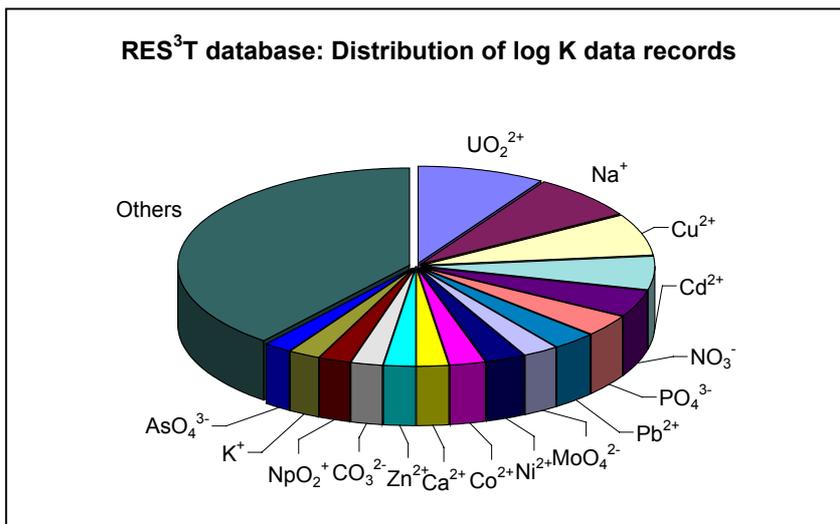


Fig. 11: Distribution of surface complexation constants records amongst ligands

The distribution of the log K data records in terms of actinides, fission and activation products is shown in Fig. 12. As can be seen most of the relevant records currently contained in the database are surface complexation constants for uranium(VI). In general there is a lack of data for the reduced oxidation states of U, Np and Pu. This means that at present the information supply is very unbalanced concerning the requirements of risk assessment and site remediation in the nuclear field.

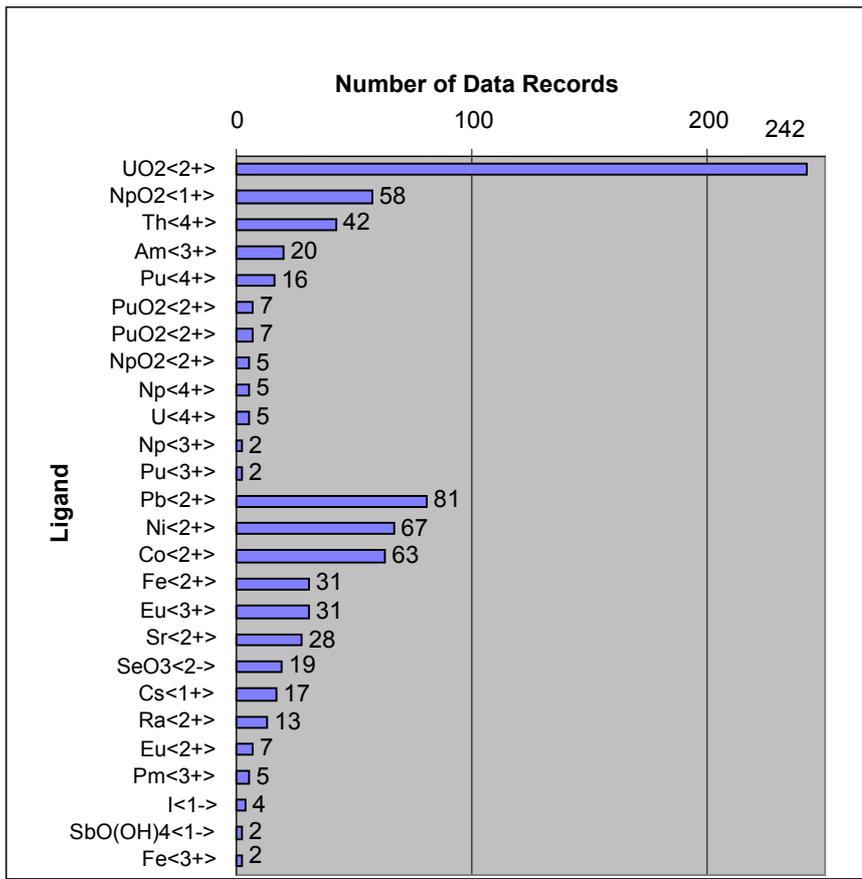


Fig. 12: Amount of surface complexation constants for actinides and relevant fission / activation products

## 5 Description of the Database

The Start Menu / Main Menu opens after starting RES<sup>3</sup>T following brief information about some local program settings. By clicking on the buttons

- Data Query & View
- Data Assembly & Formatting
- Data Input & Editing
- Administration
- General Help

the corresponding menus will be opened. A detailed description of the database RES<sup>3</sup>T is provided within in the accompanying document "RES<sup>3</sup>T Manual". Therefore only a short overview of the different menus is given here.

### 5.1 *Data Query and View*

Users can easily extract specific data sets, e.g., all records relevant for the combination of a specific mineral and a specific SCM. They can also choose to show all sorption data available for a certain element / ligand / ion, or all published surface area data of a mineral. Once a data set has been generated based on queries, it can be shown on the screen or printed out as a well formatted report. The results can also be exported into MS Excel spreadsheets for further processing.

In the Query menu, double-clicking into a scroll list field after a valid selection will give access to all details of the respective data item. Such a more detailed look at data items is also provided in the various query result view forms, here the small buttons labeled with "D" on the right hand side of the result fields.

### 5.2 *Data Assembly and Formatting*

According to the complexity of natural systems the user is given an opportunity to not only scan for a single mineral or ligand but to assemble a SCM data set for all combinations of a list of chosen minerals and a list of chosen ligands. In subsequent steps an SCM submodel must be selected to enforce at least a minimum degree of internal data consistency, and the data set can then be further refined.

The final data set can be exported into an ASCII file to be used in other geochemical speciation codes such as MINTQA2 (Allison *et al.*, 1991), GEMS (Karpov *et al.*, 1997), PHREEQC/PHREEQC-2 (Parkhurst, 1995; Parkhurst and Appelo, 1999) or HARPHRQ (Brown *et al.*, 1988) and reactive transport software such as CHEMTARD (Bennet *et al.*, 1992) or OS3D/GIMRT (Steefel and Yabusaki, 1995). Actually, this is possible as Excel spread sheet or ASCII file.

### **5.3 Data Input and Editing**

To prevent unauthorized data manipulation and the emergence of different unsynchronized database versions, the whole editing shell can be uncoupled and hidden from the user.

To ensure that all lists for input selections are properly set up during the data input procedure, a certain input order should be followed, starting with the input or update of bibliographic data (if not already correctly present). Next step would be to add the mineral, if it is still missing. Then comes the input of sample specific data, which in turn is a prerequisite for records containing site densities and surface protolysis constants. Finally, surface complexation data can be edited.

The menu "Advanced Editing" combines input masks for all auxiliary information that usually is not changed very frequently:

- SCM: Theory
- Experimental Methods
- Species: Spectroscopic Evidence (not used so far)
- Ligand Definition
- Surface Site Types
- Mineral Alteration and Kinetics (not used so far)

### **5.4 Administration**

This menu combines several database management tasks, some of them being only accessible to users with administrator privileges. Respective buttons will be grayed out for other users. These tasks are the backup of the whole database, a statistical data evaluation, the definition of an export format for bibliographic references, the definition of the path to the online manual, a routine exporting RES<sup>3</sup>T into an SQL-based file for

use in other database software such as MySQL or Oracle, and the management of various local options.

## **5.5 General Help**

Pressing the button “Help” will open the start page of an HTML-based RES<sup>3</sup>T manual, provided a web browser is already installed on the PC. Inside the manual one can navigate in the usual manner, with all the menu screenshots providing click-sensitive areas. In addition to this general help, most of the important menu forms also provide a help button in their footer section which will bring the user to a chapter of the online manual relevant for the respective menu form.

## 6 Summary

### 6.1 Results

An MS Access based digital thermodynamic sorption database has been developed and tested. This database is named “RES<sup>3</sup>T - Rossendorf Expert System for Surface and Sorption Thermodynamics”. It is mineral-specific and can therefore be used for additive models of complex solid phases such as rocks or soils. An integrated user interface helps users to access selected mineral and sorption data, to extract internally consistent data sets for sorption modeling, and to export them in formats suitable for other modeling software. Data records comprise mineral properties, specific surface area values, surface binding sites characteristics, sorption ligand information, and surface complexation reactions. An extensive bibliography is included, providing links not only to the above listed data, but also to background information concerning surface complexation model theories, evidence for surface species, and sorption experimental techniques.

As described in detail in chapter 4, the content of the database is very diverse and comprehensive. Based on 1460 literature references, up to now data records for

- 111 minerals;
- 879 sample specific data;
- 1047 protolysis data records and
- 2611 surface complexation constants

are stored inside RES<sup>3</sup>T. All these numbers are as of July 31, 2004.

The elements covered by RES<sup>3</sup>T comprises the actinides and lanthanides as well as the heavy metals and As, but also major constituents of the background media (groundwater, seepage water, solutions from corrosion processes). A statistical evaluation of the available SCM data records reveals that at present the information supply provided through the open literature is very unbalanced concerning the requirements of risk assessment and site remediation. Most SCM data are determined for the contaminants uranium, copper, cadmium, and lead, but nearly no data are available for other actinides (especially under reducing conditions). Concerning the solid phases, iron (hydr)oxides, clays, quartz varieties, aluminum (hydr)oxides, and titanium oxides are well represented, whereas important rock forming mineral groups such as feldspars, mica, pyroxenes, amphiboles, or olivines have not been investigated to a satisfactory extent. The largest data subsets are accumulated for the minerals Goethite ( $\alpha$ -

FeOOH), Ferrihydrite ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), amorphous Silica & Quartz ( $\text{SiO}_2$ ), Alumina ( $\gamma\text{-Al}_2\text{O}_3$ ), Kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), Vernadite ( $\delta\text{-MnO}_2$ ), Anatase & Rutile ( $\text{TiO}_2$ ), Montmorillonite ( $\text{Na}_{0.33}\text{Mg}_{0.33}\text{Al}_{1.67}\text{Si}_4\text{O}_{10}(\text{OH})_2$ ), and Magnetite ( $\text{Fe}_3\text{O}_4$ ). The overwhelming majority of SCM data was determined at room temperature, for any scenario coupled to elevated temperatures the database will be insufficient. Here additional experiments and the development of reliable temperature extrapolation methods is of paramount interest.

It is also interesting to analyze the experimental methods and the data processing procedures (fitting methods / codes) mainly used to obtain SCM parameters. The majority of the surface site density values originates from potentiometric titrations. Other often used methods are the tritium exchange and sorption isotherms. The potentiometric titration is the preferred experimental method for the calculation of the protolysis constants, too. In contrast, other methods, such as mean/best estimate or batch sorption experiments are negligible. About half of the surface complexation constants gathered in RES<sup>3</sup>T are obtained by batch sorption experiments. Other often used methods are the potentiometric titration method, the measurement down of sorption isotherms, or empirical correlations. Graphical methods (e.g. the double extrapolation technique) were the most often used data processing procedures for the determination of protolysis constants and surface complexation constants in the past. For the last twenty years special software has been used chiefly. This software contains routines for iterative improvement of the fit parameter and for automatic identification of compliance of convergence criteria. Especially the fit program FITEQL (Westall, 1982; Herbelin and Westall, 1996) is applied. Other programs, such as GRFIT (Ludwig, 1996), GEMS-Selector (Karpov *et al.*, 1997) and C-Letagrop (Östhols, 1994) are rarely used. The second, not so often used mainstream is the interconnection of speciation programs (with implementation of several SCM) with external parameter optimization. Speciation programs with the ability of SCM involvement are MINTEQ/MINTEQA2 (Felmy *et al.*, 1984; Allison *et al.*, 1991), MINEQL (Westall *et al.*, 1976) with successors HYDRAQL (Papelis *et al.*, 1988) and MICROQL (Westall, 1979a and b), GEOSURF (Sahai and Sverjenski, 1998), CHESS (van der Lee, 2003), HARPHRQ (Brown *et al.*, 1988) or PHREEQC (Parkhurst, 1995; Parkhurst and Appelo, 1999).

## 6.2 Application

In various papers and lectures the RES<sup>3</sup>T project team presented application examples for the RES<sup>3</sup>T database. Namely, the database helped to illustrate the current blind predictive capabilities of SCM (see the chapter “Publications” below for a respective bibliography). This will promote a more widespread use of modern sorption concepts such as surface complexation combined with surface precipitation, ion exchange and the formation of solid solutions. The systems covered in these papers are Np(V) sorption onto hematite, U(VI) sorption onto quartz, Se sorption onto goethite and Cu(II) sorption onto goethite.

Together with the database, a strategy was derived to obtain reliable and comprehensive sets of sorption data for complex natural systems. This includes approximation methods to fill crucial data gaps. Based on the information about the minerals collected in the sorption database RES<sup>3</sup>T, first a set of relevant surface species must be formed. Then respective surface complexation parameters are taken from RES<sup>3</sup>T: the binding site density for the minerals, the surface protolysis constants, and the stability constants for all relevant surface complexes. To be able to compare and average thermodynamic constants originating from different sources a normalization concept is applied. A general aim is to keep the number of parameters at a minimum, therefore the Diffuse Double Layer model is selected to account for electrostatics. The calculations were performed with the FITEQL code, version 3.2 (Herbelin and Westall, 1996).

In most cases the model prediction represented the experimental values for the sorbed amount of Np, U, Se and Cu, expressed as conventional distribution coefficients  $K_d$ , as required by Performance Assessment (PA) software within one order of magnitude or better.

As an example to illustrate the effect of parameter uncertainty in blind predictions the Np(V) sorption onto hematite was selected. None of the randomly generated pK sets parameter at the uncertainty analysis did deliver unacceptable blind predictions for the distribution coefficients. The vast majority of measured  $K_d$  values were predicted within one order of magnitude. Thus the formally large spreading of the pK values as extracted from literature (even after normalization and extrapolation to infinite dilution) is actually not critical. For well-defined mineral systems, provided a suitable database is accessible, the SCM approach seems to be very promising. This will be confirmed by further studies extending the range of minerals and contaminants.

### **6.3 Benefit and Utilization**

The mineral-specific thermodynamic sorption database RES<sup>3</sup>T enables methodical progress in the

- supply and valuation of thermodynamic sorption data;
- modeling of sorption processes for complex systems;

In combination the results allow a considerably more realistic and trustworthy description of speciation and migration of different contaminants (e.g., radionuclides, heavy metals, arsenic).

The scientific-technical benefit composed of

- first-time central provision of most SCM data published in the open literature;
- plausibility and consistency check based on original literature with backtracking of secondary references;
- creation of fundamentals for validation of data sets regarding experimental errors, consistency and model adequacy, as well as their representation for the respective minerals;
- output of sorption data sets (flexible format, fast, convenient);
- automation of data processing with transfer of specially produced data sets in EXCEL and ASCII format;
- provision of tools for conversion and computation to increase the efficiency and decrease the error possibilities, and
- identification of essential data gaps, errors, and discrepancies, supporting the planning and optimization of further experimental investigations.

The database is publicly available as CD-ROM or per e-mail as ZIP-File (res3t@fz-rossendorf.de), bundled with an installation help and an extensive manual.

### **6.4 Outlook**

The current status of the RES<sup>3</sup>T database opens the way for several future development directions. One major goal is the implementation of a world wide web (WWW) gateway to allow easy external access to the data base via the Internet. Another important activity aims at automatic data conversion between various reaction formulations to account for the different formulations for chemical master species used in speciation

codes. To close at least in a preliminary way data gaps future database releases should be supplemented by data estimation methods such as Linear Free Energy Relationships, see, e.g., Dzombak and Morel (1990). Also a future incorporation of data about the surface reactivity of the various crystal planes is anticipated.

To enlarge the application fields of RES<sup>3</sup>T by a coupling to sorption databases utilizing the  $K_d$  approach (namely the SODA database by Brasser *et al.*, 2002) would generate further benefits. A respective project proposal has been developed recently.

Whereas it has never been a goal of the present project to include also all the raw experimental data from sorption studies, this has been frequently demanded by the user community. In particular this eventually would enable the users to perform their own fitting exercises to derive model parameters. Such a task, however, would require much larger personnel and time resources than currently assigned to the project. This also holds for a large-scale incorporation of kinetic data and information of independent spectroscopic evidence for surface species, despite the fact that the corresponding table structures and input forms are already available. To approach such a challenging task probably a European-wide effort has to be launched.

## 6.5 Publications

The following publications and conference talks are summarizing results from the RES<sup>3</sup>T project:

- V. Brendler, A. Vahle, Th. Arnold, G. Bernhard, Th. Fanghänel: A mineral-specific thermodynamic sorption database. Migration 2001 Conference, Bregenz, Austria, September 16-21, 2001.
- V. Brendler, T. Arnold, A. Richter, G. Bernhard, Th. Fanghänel: RES<sup>3</sup>T - Rossendorf expert system for surface and sorption thermodynamics, 23<sup>rd</sup> Rare Earth Research Conference, Davis, California, July 14-18, 2002.
- V. Brendler, T. Arnold, A. Richter, G. Bernhard, Th. Fanghänel: From  $K_D$  to SCM: Present state of actinide data supply, International Conference and Workshop "Uranium Mining and Hydrogeology III", Freiberg, September 15-21, 2002.
- V. Brendler, T. Arnold, A. Richter: Current predictive capabilities of surface complexation models, Annual Report FZR 2002, p. 40.
- V. Brendler, A. Vahle, T. Arnold, G. Bernhard, T. Fanghänel: RES<sup>3</sup>T – Rossendorf expert system for surface and sorption thermodynamics. Journal of Contaminant Hydrology 61 (2003): 281-291.
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***Development of a Mineral-Specific Sorption  
Database for Surface Complexation Modeling***

***Entwicklung einer mineralspezifischen Sorptions-  
Datenbank für Oberflächenkomplexierungsmodelle***

**Project PtWt+E 02E9471**

Part II: Manual

*RES<sup>3</sup>T*

*Rosendorf Expert System for Surface and Sorption*

*Thermodynamics*

*1<sup>st</sup> Release*

Vinzenz Brendler, Anke Richter

Dresden, September 2004

## Disclaimer

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# 1 Introduction

RES<sup>3</sup>T is a digitized version of a thermodynamic sorption database as required for the parametrization of Surface Complexation Models (SCM). It is mineral-specific and can therefore also be used for additive models of more complex solid phases such as rocks or soils.

An integrated user interface helps to access selected mineral and sorption data, to convert parameter units, to extract internally consistent data sets for sorption modeling, and to export them into formats suitable for other modeling software. Data records comprise of mineral properties, specific surface area values, characteristics of surface binding sites and their protolysis, sorption ligand information, and surface complexation reactions.

The following sub-models are already implemented, extensions to other variants are straightforward: the Non-Electrostatic Model, the Diffuse Double Layer Model, the Constant Capacitance Model, the Triple Layer Model, the Basic Stern Model, and the 1-pK approach (CD-)MUSIC. For every SCM type (where applicable), also the concept of strong and weak binding sites is included. Surface species composed from up to two different ligands can be incorporated.

An extensive bibliography is included, providing links not only to the above listed data items, but also to background information concerning surface complexation model theories, related software for data processing and modeling, and sorption experiment techniques. Only very few of the abundant surface complexes proposed in the literature (mostly resulting just from best-fit considerations) are actually validated by spectroscopic evidence or supported by theoretical (quantum-chemical) calculations. If such information is available it is also stored in the database.

The database will help to substitute the at present in risk assessment studies most often applied simplistic distribution coefficients ( $K_d$ -values) by the more realistic description of sorption phenomena with SCM. It assists the identification of critical data gaps, the evaluation of existing parameter sets, consistency tests and the establishment of selected reference data sets. As to the knowledge of the authors, so far there is no such digital thermodynamic database for surface complexation equilibria existent world-wide, despite the vast amount of available data.

The RES<sup>3</sup>T database is intended for an international use. This requires high standards in availability, consistency and actuality. Therefore the authors of the database decided to couple the database onto an authorization tool.

This decision led to a categorizing of users into (at the moment) three groups:

- **users** that want to exploit the database for their needs by searching for data records or assembling their problem-specific data set for more complex systems. The members of that group (which is the default group) are only allowed to view, extract, and process data for output, but neither to change the database content nor its internal structure.
- **editors** that are considered qualified for the assessment of publications focused on surface complexation and related areas. In addition to the actions allowed for mere users they can add and edit most of the database records.
- **administrators** with unrestricted access to the underlying database engine. They are allowed to modify table structures and internal relationships, input and output masks and subroutines etc. They should maintain the software and provide regularly updates of the database reflecting user response (bug reports and requests for additional functionality) and project progress based on the steadily ongoing development in the field of surface complexation and related sorption phenomena (development in theories and models, advance of experimental methods).

The access to the database is controlled through user IDs and respective passwords. The assignment of users to the various groups and the provision of valid passwords is organized by the authors of the database. At present the user ID and the associated password will be sent by E-mail. Each user should have received one already, if not please contact the RES<sup>3</sup>T authors (see end of this document for contact details).

## **2 Installation**

### **2.1 RES<sup>3</sup>T Software Package**

Based on the above explained authorization philosophy, the following files are part of the RES<sup>3</sup>T distribution:

- RES3T\_2000.mdb MS Access 2000 version of the database
- RES3T\_Group.mdw file for user authorization maintenance
- RES3T.ini.example template for local initialization file
- RES3T\_Icon.ico icon for the RES<sup>3</sup>T application
- RES3T\_Readme.pdf Readme file in Adobe PDF Format
- RES3T\_Manual.pdf this document in Adobe PDF Format

### **2.2 Minimal System Requirements**

The minimal system requirements to install and run RES<sup>3</sup>T are:

- An IBM PC-compatible PC with Pentium or higher processor
- 64 MB of RAM
- 20 MB of free hard disk space
- CD-ROM drive
- MS Windows 98, NT 4 or 2000

So far, the RES<sup>3</sup>T database has been successfully tested under the Microsoft operating systems Windows NT 4, Windows 2000, and Windows 98. In principle it should also work under Windows 95, Windows ME, and Windows XP. Any information about installations on these latter three platforms are very much appreciated.

At the moment the database can only be used when there is already MS Access 2000 (part of the respective MS Office Professional Versions, but also available separately) installed on your PC. After this has been confirmed, the installation can start.

## 2.3 Program Setup

There is no setup file, so all steps must be done by hand:

- I All the files from the CD should simply be copied to a directory of your choice. If you received a compressed zip-archive, expand it into a directory. In any case, preserve the subdirectory structure.
- II Then, right-click on the file **RES3T\_2000.mdb**, select “Properties” and un-check the “Read-only” button (most probably only set for the CD version).
- III The next step is to get the user authorization running. With the default MS Access permission levels you will not be able to use RES<sup>3</sup>T, so you must make use of the **RES3T\_Group.mdw** file instead. The easiest way to run RES<sup>3</sup>T with the right permissions is to create a separate link on your desktop with the following target (see link properties sheet):

```
“Path_to Access_executable” “Path_to_RES3T_database” /Wrkgrp  
“Path_to_RES3T_groupfile”
```

All four items in this command line are separated by space. If any of the three paths contain spaces themselves you must include them into quotation marks. An example is given below, adapt it to your needs, please:

```
"D:\MSOffice\Office\MSACCESS.EXE" "I:\RES3T_2000.mdb" /Wrkgrp  
"I:\RES3T_Group.mdw"
```

- IV Each time you start RES<sup>3</sup>T, e.g., by double-clicking the icon created as described above, you will be asked for your user ID and the password. Both you should have received in a separate E-mail.
- V To be able to export database research results into MS Excel or pure ASCII format, the local path to the MS Windows notepad.exe editor, and the directories to store Excel and ASCII output files must be set. These and other settings are loaded at start from an initialization file named **res3t.ini**. An example / template for such an initialization file is provided and should be placed in the local Windows system installation directory (most often C:\WIN, C:\WINNT, or C:\WINDOWS). In case there is no initialization file available, default values will be loaded (see the chapter about “Administration” for details). Please ensure, that these default directories, or the ones defined explicitly by you in the initialization file, are really existing. At present, the online manual is only accessible as a local version, with all HTML files placed in the subdirectory named “Manual”. Therefore, the path must simply be set to “Man-

ual". Do not use the full directory path, as in contrary is required for all file export features.

The manual provides you more detailed information how to use RES<sup>3</sup>T. But keep in mind that the functionality offered by RES<sup>3</sup>T is defined by the user permissions, i.e. several features will be disabled, especially administrative tasks and all data editing, if you log in as a "general user" not belonging to the administrator group. It is required that you start RES<sup>3</sup>T from within the installation directory, otherwise the manual pages will not be found by RES<sup>3</sup>T. If you create a shortcut link to RES<sup>3</sup>T on your desktop be sure to set the working directory in the "Properties" field for this shortcut accordingly.

To uninstall the software it is sufficient to delete all the files that were copied from the RES<sup>3</sup>T CD-ROM or extracted from the zip file.

### 3 Start Menu / Main Menu

In Fig. 1 you see the main menu that pops up after starting RES<sup>3</sup>T. But before this start menu opens, a message box is shown informing about the current settings of the local options.

The following general navigation principles apply to *all* forms and menus being part of the RES<sup>3</sup>T interface:

- If one wants to select an entry from a scroll-down list the typing of one or more leading letters will scroll the list to the first matching entry.
- Entries are not case-sensitive in all input fields for search queries and in scroll-down lists.
- When the mouse moves over buttons and scroll lists, a quick tip about the purpose of that very element will pop up.
- By using the TAB key it is possible to move inside forms from one button to the next and from one input field to the next.
- Pressing the ESC key cancels all changes done so far in a form as long as it has not been saved in the meantime (explicitly or by switching to another record).

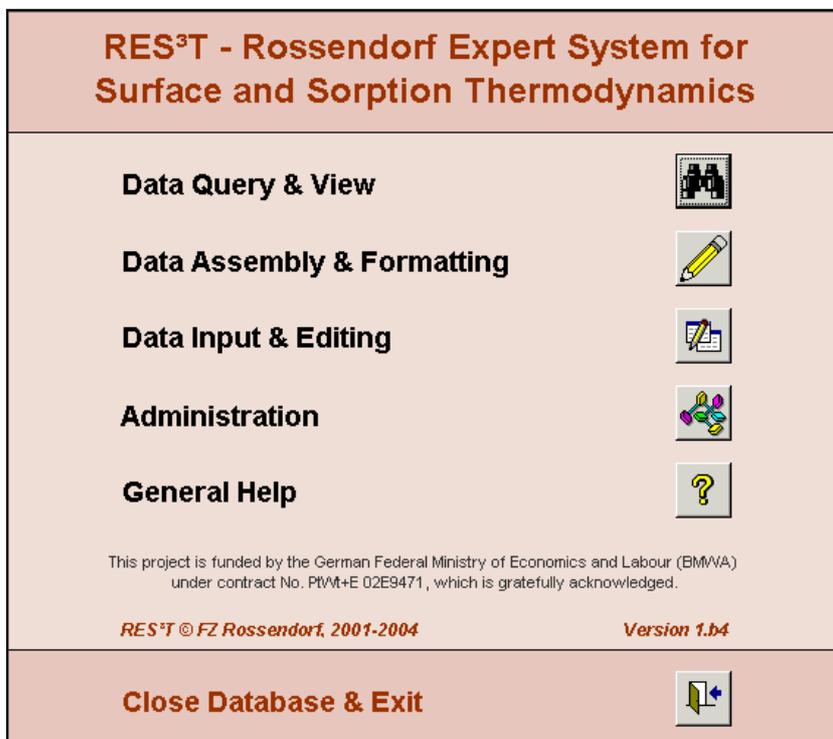


Fig. 1: Main menu of the RES<sup>3</sup>T database

### 3.1 Content policy

Both when entering or editing data records and when evaluating data query responses the user should keep in mind some general principles steering the selection, input handling and structuring of sorption data inside the RES<sup>3</sup>T framework.

- *When is a data set considered a separate record ?* At least one required parameter must be different from other data records or parameters from different other sources have been combined to a new record.
- *What is considered a "mineral" ?* This is not so clear, a look into [http://www.webmineral.com/Mineral\\_Definition.shtml](http://www.webmineral.com/Mineral_Definition.shtml) gives various mineral definitions:
  - "A mineral is an element of chemical compound that is normally crystalline and that has been formed as a result of geological processes." (Nickel, 1995)
  - "Minerals are naturally-occurring inorganic substances with a definite and predictable chemical composition and physical properties." (O'Donoghue, 1990).
  - "A mineral is a naturally occurring homogeneous solid, inorganically formed, with a definite chemical composition and an ordered atomic arrangement" (Mason et al., 1968).
  - "These... minerals ...can be distinguished from one another by individual characteristics that arise directly from the kinds of atoms they contain and the arrangements these atoms make inside them" (Sinkankas, 1966).
  - "A mineral is a body produced by the processes of inorganic nature, having usually a definite chemical composition and, if formed under favorable conditions, a certain characteristic atomic structure which is expressed in its crystalline form and other physical properties" (Dana & Ford, 1932).

See also the IMA Commission On New Minerals And Mineral Names: Procedures and Guidelines on Mineral Nomenclature (Nickel and Grice, 1998) for a technical discussion on "what is a mineral." In RES<sup>3</sup>T the first definition is followed.

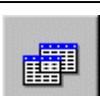
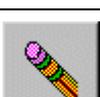
- *How to deal with inconsistent / contradictory data ?* The original published value is stored in the database anyway, but respective annotations have to be put into the comment field. Furthermore, set the status field to "deprecated" if the data are highly suspicious. There is one exception: the sign of pK and log K values will be reversed if it is obvious that they are wrong due to misprints.

- *How to deal with obviously identical data probably originating from the same source, but not cited correctly ?* Here, there are two ways to proceed: a) store data record as published but with an appropriate comment **or** b) correct / add the data source, but give an explanation in the comment
- *How to deal with literature references without any usable information ?* Put a short description of the content in the comment field, adding that there are no information directly usable for the database. Just deleting that reference may lead to a later re-occurrence (especially if the title suggests that there may be useful information in it). Furthermore, set the status field to "irrelevant".
- *How to deal with values covering various ionic strengths (IS) ?* If experiments for various ionic strengths are reported, specify the lowest one in this field and mention the other ones in the comment field (values and respective ionic strength). If the reported protolysis constants refer to an extrapolated infinite dilution, set the ionic strength to zero and specify all experimental ionic strengths in the comment field. Leave the ionic strength field blank if the extrapolation to IS=0 is not explicitly given, or if the work covers different ionic strengths and the published values can not be assigned to one of them. If there are mixed background electrolytes or experiments with different electrolytes, specify them in the comment field. The type of the background electrolyte / medium / salt can be selected from a scroll list. If not available, go back to the table "Electrolyte" (there is no extra input mask available) and add the respective medium. So far, there is no commonly agreed-upon model for activity coefficients for surface species, rendering an extrapolation of reaction constants from the experimental ionic strength to infinite dilution a very difficult task.

### **3.2 Navigation buttons**

Various navigation elements (buttons) may occur on the footer section of database forms. Clicking them will start actions as described below:

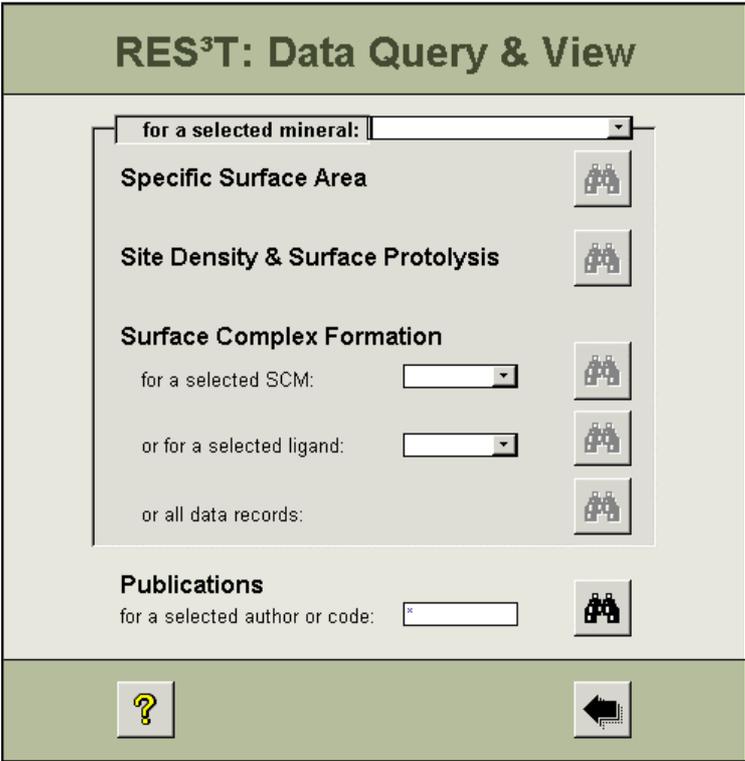
Table 1: Navigation buttons

	<b>This button will....</b>
	... open a context-sensitive HTML-based help file
	... hardcopy the form (screen dump without further questions !) 1:1 to the printer
	... generate a report for print
	... export the current form into an MS Excel spreadsheet
	... export the current form into pure ASCII text format
	... convert the bibliographic reference (ready for "Cut & Paste" into other documents) according to editorial guidelines of different journals
	... open a cross table showing available mineral-ligand combinations
	... select all data records in the list
	... cancel all data record selections in the list
	... undo the last data modification / input / deletion of the current form
	... update the display in the form after changing the content of underlying auxiliary tables
	... close the form and bring you back to the previous form or menu, functions also as "OK" button in input forms

## 4 Data Query & View

This part of the RES<sup>3</sup>T interface (see Fig. 2) ensures that users can easily extract specific data sets, e.g., all records relevant for the combination of a specific mineral and a specific SCM. They can also choose to show all sorption data available for a certain element / ligand / ion, or all published surface area data of a mineral. Once a data set has been generated based on queries, it can be shown on the screen or printed out as a nicely formatted report. The results can also be exported into MS Excel spreadsheets for further processing.

Double-clicking into a scroll list of the query form after a valid selection will give access to all details of the respective query selection. The only exception is the input field for the publication search string.



The screenshot shows the 'RES<sup>3</sup>T: Data Query & View' menu. At the top, there is a dropdown menu labeled 'for a selected mineral:'. Below this, there are three main sections, each with a list of options and a small icon of two people:

- Specific Surface Area**
- Site Density & Surface Protolysis**
- Surface Complex Formation**
  - for a selected SCM: [dropdown]
  - or for a selected ligand: [dropdown]
  - or all data records:
- Publications**
  - for a selected author or code: [input field]

At the bottom left, there is a question mark icon, and at the bottom right, there is a back arrow icon.

Fig. 2: Data Query & View menu of the RES<sup>3</sup>T database

Such a more detailed look at data items is also provided in the various query result view forms described later. There, the small buttons labeled with "D" on the right hand side of various result fields (including the query string repeated on top of the result form!) will open a form providing extra information.

## 4.1 Data for a selected mineral

As compulsory first step, a mineral from a scroll list must be selected. If this is done, some of the buttons below will turn from light gray into dark gray indicating that they are now in operation. As long as no valid mineral is selected, all buttons are inactive. Keep in mind that some minerals are quite close to each other in their surface complexation behavior, so if you do not find appropriate data for, e.g., quartz you can also look under amorphous silica. If the database does not contain data satisfying the query criteria an appropriate information box will pop up.

In case one wants to get the data not only for one mineral and/or one ligand it is advised to use the query forms presented under "Data Assembly & Formatting".

### 4.1.1 Specific Surface Area

Pressing the button "Specific Surface Area" will list all data records containing specific surface areas for the selected mineral. The columns are (from left to right): "Specific Surface Area in  $\text{m}^2/\text{g}$ ", "Reported Grain Size in  $\mu\text{m}$ ", and "Literature Reference", sorted by the area size and the literature reference code.

In Fig. 3 you can see the query results for an example: the specific surface area of quartz.

Specific Surface Area in $\text{m}^2/\text{g}$	Reported Grain Size in $\mu\text{m}$	Literature Reference
0.01	75-150	CMBMH02
0.01	106-180	T94
0.028		J71
0.03		BPTA96
0.03	150-250	PTBP98
0.08	125-250	MSHV896
0.1	63-200	AZBN98
0.1	200-700	REDCD00
0.1	106-180	T93
0.1	<2	VT98

Fig. 3: Query results of surface data for "Quartz"

### 4.1.2 Site Density & Protolysis

Pressing the button "Site Density & Protolysis" will list all data records containing surface binding site densities and site protolysis constants for the selected mineral. The columns are (from left to right): "Site Type", "Site Density in sites /  $\text{nm}^2$ ", "pK1

Exp./Norm.", "pK2 Exp./Norm.", "PZC", "C1", "SCM Type", and "Literature Reference", sorted by the SCM type and the literature reference code. Fig. 4 shows the query results of site density and surface protolysis data for quartz.

All site density values presented are already converted from the original unit into sites / nm<sup>2</sup>. If one is interested in the originally published value, a double-click on the "D" button (located right to the "C1" column) will lead to the respective detailed data record.

**RES<sup>3</sup>T: List of Site Density and Surface Protolysis Data**

for:

pK1: -log K of 1st deprotonation (  $\gg X-OH_2^+ \rightleftharpoons \gg X-OH + H^+$  )  
pK2: -log K of 2nd deprotonation (  $\gg X-OH \rightleftharpoons \gg X-O^- + H^+$  )

Site Type	Site Density in sites / nm <sup>2</sup>	pK1		pK2		PZC	C1	SCM Type	Literature Reference
		Exp.	Norm.	Exp.	Norm.				
»Si-OH	3.00						2.50	r ?	r BL82
»Si-OH	11.40							r ?	r G76
»Si-OH	6.30							r ?	r G76
»Si-OH	4.65			7.50	7.91		3.9	r 1pK-BS	r MSHVB96
»Si-OH	8.00	-3.50	-3.68	7.50	7.68	2.00	3.9	r BS	r HV90
»Si-OH	3.77							r BS	r P02b
»Si-OH	2.96							r BS	r P02b
»Si-OH	5.99							r BS	r P02b
»Si-OH	10.00	-3.30	-3.38	9.30	9.38	3.00	1	r CC	r SS96a
»Si-OH		-1.90		11.90				r CDM	r HVB89a
»Si-doublu		-16.90						r CDM	r HVB89a

Datensatz: 1 von 54

Fig. 4: Query results of site density and surface protolysis data for "Quartz"

As clearly pointed out by Kulik (2002), the establishment of standard and reference states for surface complexation data is essential for a proper thermodynamic handling of such reactions. Therefore a respective normalization procedure has been integrated into RES<sup>3</sup>T, allowing a comparison of the various SCM parameters for given combinations of SCM subtype and mineral. Following Kulik and setting the reference site density to 12.05 sites / nm<sup>2</sup> (=20mmol / m<sup>2</sup>), the protolysis constants are normalized according the following equations, where  $\Gamma_{exp}$  is the experimentally determined surface site density:

$$pK1_{norm} = pK1_{exp} + \log \frac{\Gamma_{exp}}{12.05} \quad pK2_{norm} = pK2_{exp} - \log \frac{\Gamma_{exp}}{12.05}$$

These normalized values are shown accordingly in the columns labeled with "pK# Norm.", next to the original value corresponding to the experimental site density.

### 4.1.3 Surface Complex Formation

#### Surface Complex Formation - for a selected SCM

The respective button is only activated when both a valid mineral and a valid surface complexation model is selected. It lists all data records containing surface complex formation constants for the selected combination of SCM and mineral. The columns are (from left to right): "1st Ligand", "Chemical Equation", "log K Exp./Norm.", and "Literature Reference", sorted by ligand formula and reaction equation. As for the "Site Density & Protolysis" form, the columns for log K correspond to the experimental value and the one normalized to a site density of 12.05 nm<sup>2</sup>.

$$\log K = \log K_{\text{exp}} + \log \frac{\Gamma_{\text{exp}}}{12.05}$$

The query results of surface complexation data for quartz with the Triple Layer Model are shown in Fig. 5.

1st Ligand	Chemical Equation	log K Exp. / Norm.	Literature Reference
Ca<2+>	2 *Si-OH + Ca<2+> = (*Si-O)2-Ca + 2 H<1+>	-2.50 -2.90	H94
UO2<2+>	2(*Si-O 0.5 H) + UO2<2+> + H2CO3 + H2O = *Si2-O-UO2-OHC03	-19.00 -19.42	K02b
Na<1+>	*Si-O 0.5 H + Na<1+> = *Si-O-0.5 Na + H<1+>	-7.40 -7.82	K02b
NO3<1->	*Si-O 0.5 H + NO3<1-> + H<1+> = *Si-O-0.5H2NO3	-0.40 -0.82	K02b
UO2<2+>	2(*Si-O 0.5 H) + UO2<2+> = *Si2-O-UO2 + 2 H<1+>	-7.50 -7.92	K02b
UO2<2+>	2(*Si-O 0.5 H) + UO2<2+> + 2H2O = *Si2-O-UO2(OH)2<2+> + 4 H<1+>	-17.80 -18.22	K02b
UO2<2+>	2(*Si-O 0.5 H) + UO2<2+> + H2CO3 + 2H2O = *Si2-O-UO2(OH)2 CC	-24.90 -25.32	K02b
UO2<2+>	2(*Si-O 0.5 H) + 2UO2<2+> + H2O = *Si2-O-(UO2)2-OH+ + 3 H<1+>	-10.10 -10.52	K02b
UO2<2+>	2(*Si-O 0.5 H) + UO2<2+> + H2O = *Si2-O-UO2-OH<1-> + 3 H<1+>	-12.22 -12.64	K02b
NpO2<1+>	*Si-OH + NpO2<1+> = *Si-O-NpO2 + H<1+>	-6.93 -7.65	KHL99
Na<1+>	*Si-OH + Na<1+> = *Si-O-Na + H<1+>	-0.72 -1.10	KYMN96
Cs<1+>	*Si-OH + Cs<1+> = *Si-O-Cs + H<1+>	2.95 2.57	KYMN96
Na<1+>	*Si-OH + Na<1+> = *Si-O-Na + H<1+>	1.23 0.85	KYMN96

Fig. 5: Query results of surface complexation data for "Quartz" with "Triple Layer Model"

#### Surface Complex Formation - for a selected ligand

The respective button is only activated when both a valid mineral and a valid ligand is selected. It lists all data records containing surface complex formation constants for the selected combination of ligand and mineral. The columns are (from left to right): "SCM Type", "Chemical Equation", "log K Exp./Norm.", and "Literature Reference" (see Fig. 6), sorted by SCM type and literature reference code.

**RES<sup>3</sup>T: List of Surface Complexation Data**

for:  with:  as major ligand

SCM Type	Chemical Equation	log K Exp. / Norm.	Literature Reference
DDL	$\text{Si-OH} + \text{UO}_2^{2+} = \text{Si-O-UO}_2^{+} + \text{H}^{+}$	0.30 -0.42	PTBP98
DDL	$\text{Si-OH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{Si-O-UO}_2(\text{OH}) + 2 \text{H}^{+}$	-5.65 -6.37	PTBP98
DDL	$\text{Si-OH} + 3 \text{UO}_2^{2+} + 5 \text{H}_2\text{O} = \text{Si-O-(UO}_2)_3(\text{OH})_5 + 6 \text{H}^{+}$	-16.75 -17.47	PTBP98
DDL	$2 \text{Si-OH} + \text{UO}_2^{2+} = \text{Si-O-UO}_2 + 2 \text{H}^{+}$	-5.51 -5.91	AZZBN01
DDL	$\text{Si-OH} + \text{UO}_2^{2+} = \text{Si-O-UO}_2^{+} + \text{H}^{+}$	-0.30 -1.02	PJTP01
DDL	$\text{Si-OH} + \text{UO}_2^{2+} + 3 \text{H}_2\text{O} = \text{Si-O-UO}_2^{+} + 4 \text{H}^{+}$	-18.70 -19.42	PJTP01
DDL	$2 \text{Si-OH} + \text{UO}_2^{2+} = \text{Si-O-UO}_2 + 2 \text{H}^{+}$	-5.72	AZBN00a
NE	$\text{Si(w)-OH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{Si(w)-O-UO}_2(\text{OH}) + 2 \text{H}^{+}$	-4.64 -5.92	DK01
NE	$\text{Si(w)-OH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{Si(w)-O-UO}_2(\text{OH}) + 2 \text{H}^{+}$	-5.28 -6.56	DK01
NE	$\text{Si(s)-OH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{Si(s)-O-UO}_2(\text{OH}) + 2 \text{H}^{+}$	-2.56 -5.60	DK01
NE	$\text{Si(w)-OH} + \text{UO}_2^{2+} + \text{H}_2\text{CO}_3 = \text{Si(w)-O-UO}_2\text{CO}_3 + 3 \text{H}^{+}$	-6.50 -7.78	DK01
NE	$\text{Si(w)-OH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{Si(w)-O-UO}_2(\text{OH}) + 2 \text{H}^{+}$	-4.95 -6.22	DK01
NE	$\text{Si(s)-OH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{Si(s)-O-UO}_2(\text{OH}) + 2 \text{H}^{+}$	-2.19 -6.41	DK01

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Fig. 6: Query results of surface complexation data for "Quartz" with "UO<sub>2</sub><sup>2+</sup>"

### Surface Complex Formation - all data records

This button lists surface complex formation constants for the selected mineral, covering all ligands. The columns are (from left to right): "SCM Type", "1st Ligand", "Chemical Equation", "log K Exp./Norm.", and "Literature Reference" (see Fig. 7), sorted by SCM type, ligand formula, and literature reference code.

**RES<sup>3</sup>T: List of Surface Complexation Data**

for:

SCM Type	1st Ligand	Chemical Equation	log K Exp. / Norm.	Literature Reference
DDL	UO2<2+>	$2 \text{Si-OH} + \text{UO}_2^{2+} = \text{Si-O-UO}_2 + 2 \text{H}^{+}$	-5.72	AZBN00a
DDL	UO2<2+>	$2 \text{Si-OH} + \text{UO}_2^{2+} = \text{Si-O-UO}_2 + 2 \text{H}^{+}$	-5.51 -5.91	AZZBN01
DDL	Ba<2+>	$\text{Si-OH} + \text{Ba}^{2+} = \text{Si-O-Ba}^{+} + \text{H}^{+}$	-0.97	KFYNM99
DDL	Sr<2+>	$\text{Si-OH} + \text{Sr}^{2+} = \text{Si-O-Sr}^{+} + \text{H}^{+}$	-1.23	KFYNM99
DDL	Eu<3+>	$\text{Si-OH} + \text{Eu}^{3+} = \text{Si-O-Eu}^{2+} + \text{H}^{+}$	4.55	KFYNM99
DDL	Am<3+>	$\text{Si-OH} + \text{Am}^{3+} = \text{Si-O-Am}^{2+} + \text{H}^{+}$	5.07	KFYNM99
DDL	UO2<2+>	$\text{Si-OH} + \text{UO}_2^{2+} = \text{Si-O-UO}_2^{+} + \text{H}^{+}$	-0.30 -1.02	PJTP01
DDL	UO2<2+>	$\text{Si-OH} + \text{UO}_2^{2+} + 3 \text{H}_2\text{O} = \text{Si-O-UO}_2^{+} + 4 \text{H}^{+}$	-18.70 -19.42	PJTP01
DDL	UO2<2+>	$\text{Si-OH} + \text{UO}_2^{2+} = \text{Si-O-UO}_2^{+} + \text{H}^{+}$	0.30 -0.42	PTBP98
DDL	UO2<2+>	$\text{Si-OH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{Si-O-UO}_2(\text{OH}) + 2 \text{H}^{+}$	-5.65 -6.37	PTBP98
DDL	UO2<2+>	$\text{Si-OH} + 3 \text{UO}_2^{2+} + 5 \text{H}_2\text{O} = \text{Si-O-(UO}_2)_3(\text{OH})_5 + 6 \text{H}^{+}$	-16.75 -17.47	PTBP98
DDL	Na<1+>	$\text{Si-OH} + \text{Na}^{+} = \text{Si-O-Na} + \text{H}^{+}$	5.61	TZ02
DDL	Pu<4+>	$\text{Si-OH} + \text{Pu}^{4+} + \text{H}_2\text{O} = \text{Si-O-Pu}(\text{OH})_2 + 2 \text{H}^{+}$	-4.21 -4.93	WAT01b
DDL	Am<3+>	$\text{Si-OH} + \text{Am}^{3+} = \text{Si-O-Am}^{2+} + \text{H}^{+}$	-0.23 -0.95	WAT01b
NE	UO2<2+>	$\text{Si(w)-OH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{Si(w)-O-UO}_2(\text{OH}) + 2 \text{H}^{+}$	-4.64 -5.92	DK01
NE	UO2<2+>	$\text{Si(w)-OH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{Si(w)-O-UO}_2(\text{OH}) + 2 \text{H}^{+}$	-5.28 -6.56	DK01
NE	UO2<2+>	$\text{Si(s)-OH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{Si(s)-O-UO}_2(\text{OH}) + 2 \text{H}^{+}$	-2.56 -5.60	DK01
NE	UO2<2+>	$\text{Si(w)-OH} + \text{UO}_2^{2+} + \text{H}_2\text{CO}_3 = \text{Si(w)-O-UO}_2\text{CO}_3 + 3 \text{H}^{+}$	-6.50 -7.78	DK01

Datensatz: 1 von 97

Fig. 7: Query results summarizing surface complexation data for "Quartz"

## 4.2 Publications

The query field can contain either part of the name of an author or part of a (mnemonic) literature reference code. An asterisk (\*) can be used as wildcard for the search string. The columns of the result list are (from left to right): "Reference Code", "Author(s)", "Title" (below the authors), and "Year", sorted by the literature reference code. Below the reference code, the hard copy number is shown, but this is for internal use only and may be removed later. Fig. 8 shows the query results for the author "Davis".

**RES<sup>3</sup>T: Selected Data References**

Search string was: *Davis*

Reference Code	Author(s) Title	Year
ASD04	Arai Y, Sparks LD, Davis JA <i>Effects of Dissolved Carbonate on Arsenate Adsorption and Surface Speciation at the Hea...</i>	2004
BRD01	Bargar JR, Reitmeyer R, Davis JA <i>Spectroscopic characterization of U(VI)-carbonate surface complexes on hematite and fer...</i>	2001
BRD99	Bargar JR, Reitmeyer R, Davis JA <i>Spectroscopic confirmation of uranium(VI)-carbonate adsorption complexes on hematite</i>	1999
V911		
BRLD00	Bargar JR, Reitmeyer R, Lenhart JJ, Davis JA <i>Characterization of U(VI)-carbonate ternary complexes on hematite: EXAFS and electrochem...</i>	2000
V1177		
CDKK01	Curtis GP, Davis JA, Kohler M, Kent DB <i>Reactive transport modeling of uranium(VI) migration through quartz porous media under v...</i>	2001
Anke		
CFD95	Coston JA, Fuller CC, Davis JA <i>Pb<sup>2+</sup> and Zn<sup>2+</sup> adsorption by a natural aluminum- and iron-bearing surface coating on a s...</i>	1995
V1815		
CFKD02	Curtis GP, Fox P, Kohler M, Davis JA <i>Comparison of field uranium Kd values with a laboratory surface complexation model</i>	2002
V1660		
CFKD04	Curtis GC, Fox P, Kohler M and Davis JA <i>Comparison of in situ uranium Kd values with a laboratory determined surface complexation</i>	2004

Buttons: Surface Area, Site Density / Protolysis, Complex Formation

Datensatz: 1 von 57

Fig. 8: Query results of data references of "Davis"

Marking an entry from the list of search results allows to check for parameter sets stemming from that very source, namely records for specific surface areas, for site densities & protolysis constants, or for surface complexation constants. This is performed by pressing the respective smaller buttons in the middle of the form footer.

## 5 Data Assembly & Formatting

According to the complexity of natural systems the user is given an opportunity to not only scan for a single mineral or ligand but to assemble a SCM data set for all combinations of a list of chosen minerals and a list of chosen ligands. In subsequent steps after screening the overall available data records, an SCM sub-model must be selected to enforce at least a minimum degree of internal data consistency, and the data set can then be further refined. The definition and selection of the data collection must exactly follow the given order. As long as a previous step is not accomplished all further buttons are inactive, indicated by a light gray color of the respective buttons, see Fig. 9.

The final data set can be exported in a file to be used in other geochemical speciation codes such as MINTQA2 (Allison et al., 1991), GEMS (Karpov et al., 1997), PHREEQC-2 (Parkhurst and Appelo, 1999) or HARPHRQ (Brown et al., 1988) and reactive transport software such as CHEMTARD (Bennet et al., 1992) or OS3D/GIMRT (Steeffel and Yabusaki, 1995). In case of such data exports, the output format will automatically be adapted to the specific requirements of the different software packages. This feature, however, is not implemented yet. Instead, output into a general ASCII format is provided, which can easily be transformed in the required speciation input format.



Fig. 9: Data Assembly & Formatting menu of the RES<sup>3</sup>T database

## 5.1 Mineral Set Assembly

An alphabetically sorted list of all minerals is presented, where the user can make multiple selections through the check boxes on the right side of the mineral names. Here the iron containing minerals ferrihydrite, goethite, hematite are selected, see Fig. 10. There are two buttons below the table that either select all (checkbox button) or none (rubber button) entries. When all desired minerals are selected, the “Back” button must be pushed to advance to the next step in the “Data Assembly & Formatting” menu.

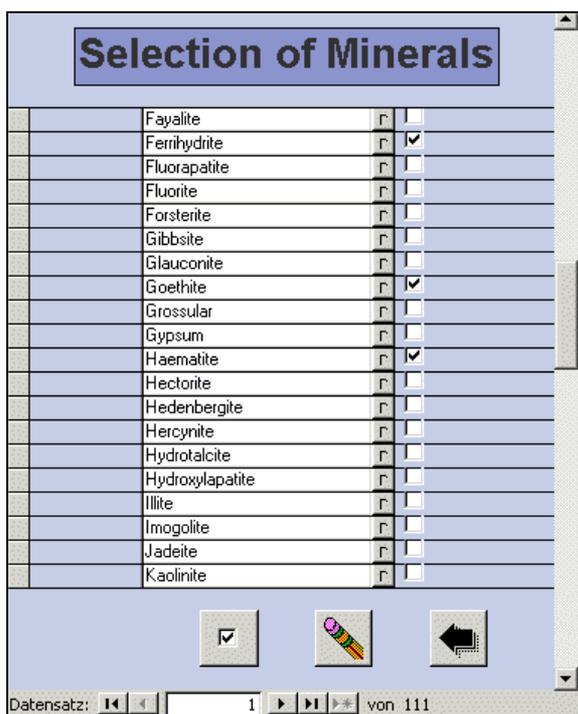


Fig. 10: Selection of minerals

## 5.2 Ligand Set Assembly

An alphabetically sorted list of all ligands is presented, where the user can make multiple selections through the check boxes on the right side of the ligand names. As an example the heavy metals cadmium, cobalt, copper, nickel, lead and zinc were selected as sorbing contaminants, see Fig. 11.

There are two buttons below the table that either select all (checkbox button) or none (rubber button) entries. When all desired ligands are selected, again the “Back” button must be pushed to advance to the next step in the “Data Assembly & Formatting” menu.

	Ligand	n	Selection
	Ca<2+>	n	<input type="checkbox"/>
	carb<1->	n	<input type="checkbox"/>
	cat<2->	n	<input type="checkbox"/>
	Cd<2+>	n	<input checked="" type="checkbox"/>
	CDTA<4->	n	<input type="checkbox"/>
	cit<2->	n	<input type="checkbox"/>
	citH<3->	n	<input type="checkbox"/>
	Cl<1->	n	<input type="checkbox"/>
	ClO4<1->	n	<input type="checkbox"/>
	CN<1->	n	<input type="checkbox"/>
	Co<2+>	n	<input checked="" type="checkbox"/>
	Co<3+>	n	<input type="checkbox"/>
	CO3<2->	n	<input type="checkbox"/>
	Cr<3+>	n	<input type="checkbox"/>
	CrO4<2->	n	<input type="checkbox"/>
	Cs<1+>	n	<input type="checkbox"/>
	Cu<2+>	n	<input checked="" type="checkbox"/>
	EDTA<4->	n	<input type="checkbox"/>
	en<0>	n	<input type="checkbox"/>
	Eu<2+>	n	<input type="checkbox"/>
	Eu<3+>	n	<input type="checkbox"/>
	F<1->	n	<input type="checkbox"/>

Datensatz: 113 von 113

Fig. 11: Selection of ligands

### 5.3 Inspection + SCM Choice

This form lists all relevant data records based on the user selections for minerals and ligands. The first column on the left specifies the applied SCM sub-model, then the mineral follows. For each surface complex formation data record also the associated experimental specific surface area and site densities are given. Then three columns follow given the protolysis constants and the complex formation constant, all normalized to the standard site density of  $12.05 \text{ nm}^{-2}$ . The next fields give the chemical reaction and the literature reference. The results are sorted by SCM type, literature reference code, and mineral name, see Fig. 12.

At the bottom of the form the button showing two tables will open a cross table giving the number of data records per combination of mineral and ligand.

Finally, the user then has to decide which SCM sub-model the assembled data set should be based on. This may of course drastically reduce the number of data records but is a requirement for an internally consistent data collection. The SCM is to be selected from the scroll list at the bottom of the form, then the "Back" button can be pressed.

Global Overview of Data Collection								
SCM Type	Mineral	Area in m <sup>2</sup> /g	Sites /nm <sup>2</sup>	normalized			Chemical Equation	Literature Reference
				pK_1	pK_2	logK		
1pK-BS	Ferrihydrite	182					2 $\text{Fe-OH} + \text{Zn}^{2+} + \text{H}_2\text{O} = \text{Fe-O-ZnOH}_2\text{C}1+ + 2 \text{H}^+1+$	DM86
1pK-BS	Ferrihydrite	182					2 $\text{Fe-OH} + \text{Cd}^{2+} + \text{H}_2\text{O} = \text{Fe-O-CdOH}_2\text{C}1+ + 2 \text{H}^+1+$	DM86
1pK-BS	Haematite	6.36	10.00	8.32		-13.98	$\text{FeOH}0.5 + \text{Co}^{2+} + 2\text{H}_2\text{O} = \text{FeOH-Co(OH)}_2\text{0.5} + 2\text{H}^+$	GJEA00
1pK-BS	Haematite	6.36	10.00	8.32		6.62	$\text{FeOH}0.5 + \text{Co}^{2+} = \text{FeOH-Co}1.5+$	GJEA00
1pK-BS	Ferrihydrite	182					$\text{Fe-singly-OH}1/2 + \text{Cd}^{2+} + \text{H}_2\text{O} = \text{Fe-singly-OH-Cd(OH)}$	VDKB87
1pK-BS	Haematite	26.5					$\text{Fe-singly-OH}1/2 + \text{Cd}^{2+} + \text{H}_2\text{O} = \text{Fe-singly-OH-Cd(OH)}$	VDKB87
1pK-BS	Goethite	95	6.00	9.00		6.20	$\text{Fe-OH}1/2 + \text{Cd}^{2+} = \text{Fe-OH-Cd}3/2+$	VHV96a
BS	Ferrihydrite	182					2 $\text{Fe-OH} + \text{Zn}^{2+} + \text{H}_2\text{O} = \text{Fe-O-ZnOH}_2\text{C}1+ + 2 \text{H}^+1+$	DM86
BS	Ferrihydrite	182					$\text{Fe-OH}_2\text{C}1+ + \text{Cd}^{2+} + \text{H}_2\text{O} = \text{Fe-O-CdOH}_2\text{C}1+ + 2 \text{H}^+$	DM86
BS	Ferrihydrite	182					$\text{Fe-OH} + \text{Cd}^{2+} + \text{H}_2\text{O} = \text{Fe-O-Cd(OH)} + \text{H}^+1+$	VDKB87
BS	Haematite	26.5					$\text{Fe-OH} + \text{Cd}^{2+} + \text{H}_2\text{O} = \text{Fe-O-Cd(OH)} + \text{H}^+1+$	VDKB87
BS	Goethite	95	4.20	8.84		5.54	$\text{Fe-OH} + \text{Cd}^{2+} = \text{Fe-O-Cd}1+ + \text{H}^+1+$	VHV96a
BS	Goethite	95	4.20	8.84		6.54	$\text{Fe-OH} + \text{Cd}^{2+} = \text{Fe-O-Cd}1+ + \text{H}^+1+$	VHV96a
CC	Ferrihydrite	193	27.00	5.35	9.05	-2.79	$\text{Fe-OH} + \text{Cd}^{2+} = \text{Fe-O-Cd}1+ + \text{H}^+1+$	AB90b
CC	Ferrihydrite	193	27.00	5.35	9.05	-2.33	$\text{Fe-OH} + \text{Zn}^{2+} = \text{Fe-O-Zn}1+ + \text{H}^+1+$	AB90b
CC	Goethite	49.6	1.20	6.17	10.88	-3.29	$\text{Fe-OH} + \text{Cd}^{2+} = \text{Fe-O-Cd}1+ + \text{H}^+1+$	AWJ99b
CC	Goethite	49.6	1.20	6.17	10.88	-13.11	$\text{Fe-OH} + \text{Cd}^{2+} + \text{H}_2\text{O} = \text{Fe-O-Cd(OH)} + 2 \text{H}^+1+$	AWJ99b
CC	Goethite	49.6	1.20	6.17	10.88	-3.66	$\text{FeOH} + \text{Co}^{2+} = \text{FeO-Co} + \text{H}^+$	AWJ99b
CC	Goethite	49.6	1.20	6.17	10.88	-11.74	$\text{FeOH} + \text{Co}^{2+} + \text{H}_2\text{O} = \text{FeO-CoOH} + 2\text{H}^+$	AWJ99b
CC	Ferrihydrite	182	3.54	6.07	9.63	3.57	$\text{FeOH} + \text{Pb}^{2+} + 2 \text{H}_2\text{O} = \text{Fe(OH)}_3(\text{s}) + \text{Pb(OH)}_2 + \text{H}^+$	FDM85
CC	Ferrihydrite	182	3.54	6.07	9.63	-0.73	$\text{FeOH} + \text{Zn}^{2+} + 2 \text{H}_2\text{O} = \text{Fe(OH)}_3(\text{s}) + \text{Zn(OH)}_2 + \text{H}^+$	FDM85
CC	Ferrihydrite	182	3.54	6.07	9.63	-0.93	$\text{FeOH} + \text{Cd}^{2+} + 2 \text{H}_2\text{O} = \text{Fe(OH)}_3(\text{s}) + \text{Cd(OH)}_2 + \text{H}^+$	FDM85
CC	Ferrihydrite	182	3.54	6.07	9.63	1.57	$\text{FeOH} + \text{Cu}^{2+} + 2 \text{H}_2\text{O} = \text{Fe(OH)}_3(\text{s}) + \text{Cu(OH)}_2 + \text{H}^+$	FDM85

Fig. 12: Global overview and data collection

## 5.4 Final Data Selection

Based on the above made user decisions (as an example the DDL model was selected) the remaining set of data records is shown, with the following fields (from left to right): mineral, specific surface area, site density, protolysis constants, chemical equation (delivering also information about the ligand), surface complex formation constant, and literature reference. The table is sorted by literature reference code and mineral name, see Fig. 13. All constants are normalized to the reference site density.

Now the user can check (using the boxes on the far right side of the table) which of the records actually should be included into the final data set. Suspicious records can be rejected, e.g., or in case of several competing values for the same surface reaction an appropriate choice can be made. To assist these decisions, the small buttons on the right hand side of the data fields labeled with "D" give access to a more detailed view of the data record, similar to the query result forms. There are two buttons below the table that either select all (checkbox button) or none (rubber button) entries.

Final Data Selection										
SCM Type:		pK and log K values are all normalized to the reference state !								
Mineral	Area in m <sup>2</sup> /g	Sites /nm <sup>2</sup>	pK_1	pK_2	Chemical Equation	logK	Literature Reference	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Goethite	79.40	1.40	6.75	9.25	»Fe-OH + Cu<2+> = »Fe-O-Cu<1+> + H<1+>	1.28	AD96c	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Goethite	79.40	1.40	6.75	9.25	»Fe-OH + Cu<2+> + SO4<2-> = »Fe-OH-CuSO4	8.75	AD96c	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Ferrihydrite	600.00	2.26	6.56	9.66	»Fe(w)-OH + Pb<2+> = »Fe(w)-O-Pb<1+> + H<1+>	0.50	APGV94	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Ferrihydrite	600.00	2.26	6.56	9.66	»Fe(w)-OH + Cd<2+> = »Fe(w)-O-Cd<1+> + H<1+>	-2.55	APGV94	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Ferrihydrite	600.00	2.26	6.56	9.66	»Fe(w)-OH + Co<2+> = »Fe(w)-O-Co<1+> + H<1+>	-1.91	APGV94	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Goethite	21.40	2.30	7.18	11.22	»Fe-OH + Cu<2+> = »Fe-O-Cu<1+> + H<1+>	2.21	BHXBS02	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Goethite	21.40	2.30	7.18	11.22	»Fe-OH + Cd<2+> = »Fe-O-Cd<1+> + H<1+>	-0.90	BHXBS02	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Goethite	21.40	2.30	7.18	11.22	»Fe-OH + Ni<2+> = »Fe-O-Ni<1+> + H<1+>	45.28	BHXBS02	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Ferrihydrite	600.00	0.06	4.96	11.26	»Fe(s)-OH + Ni<2+> = »Fe(s)-O-Ni<1+> + H<1+>	-1.46	BKEC94	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Ferrihydrite	600.00	2.26	6.56	9.66	»Fe(w)-OH + NIEDTA<2-> + H<1+> = »Fe(w)-EDTANi<1+> + H<1+>	7.65	BKEC94	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Ferrihydrite	600.00	2.26	6.56	9.66	»Fe(w)-OH + Ni<2+> + EDTA<4-> + H<1+> = »Fe(w)-NIEDTA<2-> + H<1+>	28.03	BKEC94	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Haematite	19.00	1.22	6.43	9.17	»Fe-OH + Co<2+> = »Fe-O-Co<1+> + H<1+>	-6.00	C96	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Haematite	8.00	1.20			»Fe-OH + Co<2+> + H2O = »Fe-O-Co(OH) + 2H<1+>	-14.20	C96	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Ferrihydrite	600.00	0.06	4.96	11.26	»Fe(s)-OH + Pb<2+> = »Fe(s)-O-Pb<1+> + H<1+>	2.32	DM90	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Ferrihydrite	600.00	0.06	4.96	11.26	»Fe(s)-OH + Zn<2+> = »Fe(s)-O-Zn<1+> + H<1+>	-1.34	DM90	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Ferrihydrite	600.00	2.26	6.56	9.66	»Fe(w)-OH + Zn<2+> = »Fe(w)-O-Zn<1+> + H<1+>	-2.72	DM90	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Ferrihydrite	600.00	0.06	4.96	11.26	»Fe(s)-OH + Cd<2+> = »Fe(s)-O-Cd<1+> + H<1+>	-1.86	DM90	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Fig. 13: Final data selection

The data tables can also be formatted for a report or exported into MS Excel or pure ASCII format with the help of the buttons in the lower left corner of the form. This of course will only work if some data records really have been selected through their checkboxes. The output files will be placed in the directories specified under the entries "ExcelPath" or "ASCIIPath", respectively, of the "Local Options". Furthermore it is required to give the correct path to a simple ASCII editor program under the entry "Notepad", also as part of the "Local Options". A good example for such an editor is the standard MS Windows notepad. More about meaning and handling of "Local Options" can be found under the "Administration" menu.

### 5.5 Speciation Code

Here, the user specifies the software (geochemical speciation or reactive transport) defining the output format of the final data set and to be selected from a scroll list.

### 5.6 Export it!

Pressing this button eventually triggers the export of the assembled data set into an ASCII file with the before defined format. This feature is not implemented yet.

## 6 Data Input & Editing

To prevent unauthorized data manipulation and the emergence of different unsynchronized database versions, the whole editing shell can be uncoupled and hidden from the user. This is the default for users not having administrative permissions.

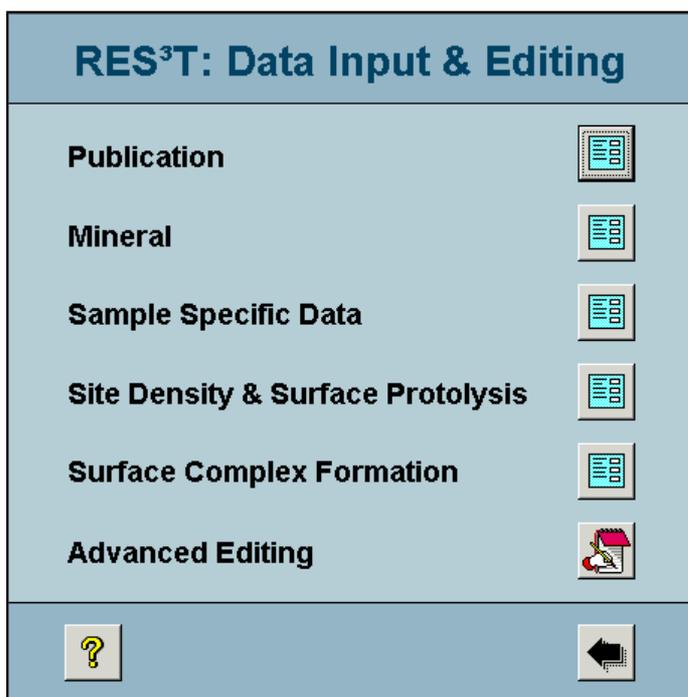


Fig. 14: Data Input & Editing menu of the RES<sup>3</sup>T database

To ensure that all lists for input selections are properly set up during the data input procedure, a certain input order should be followed, starting with the input or update of bibliographic data (if not already correctly present). Next step would be to add the mineral, if it is still missing. Then comes the input of specific surface area values, which in turn is a prerequisite for records containing site densities and surface protolysis constants. Finally, surface complexation data can be edited. This order is also reflected by the layout of the "Data Input & Editing" menu form as shown in Fig. 14.

When an input field has a pale yellow background color this indicates that an entry into this field is compulsory. Leaving such fields empty is not possible, the database will not allow to store such incomplete data records.

A remark to bibliographic references required by nearly all input forms: A selection as "Original Publication" always means really the work where the data record has been published first. If the information can only be derived from a secondary reference, then the latter must be specified in "Citation in". When later the original reference becomes available the citation entry can be removed (or moved to the comments).

The following book-keeping information apply to all forms being part of the input interface. They may be deleted / hidden for external users in later revisions.:

- Internal Status: This field gives information about the internal processing status of a given data record.
- Last Modification: These fields specify the time and date of the last modification of the given data record, and who of the registered users did it. Pressing the small button on the right of this field (showing a clock) will set the modification-stamp of that record to the current time and user.

## 6.1 Publication

This input form organizes the storage of any bibliographic information relevant for the RES<sup>3</sup>T database. Depending on the selection made in the field "Type" certain input fields may be shown or not, thus limiting the available fields (see below for a complete list) to the necessary ones. Fig. 15 shows the form layout for the publication type "Article".

The screenshot shows a web-based form titled "RES<sup>3</sup>T: Publication". At the top right, the LID is 2089. The form contains the following fields and values:

- Author(s): Payne TE, Davis JA, Lumpkin GR, Chisari R and Waite TD
- Title: Surface complexation model of uranyl sorption on Georgia kaolinite
- Year: 2004
- Mnemonic Code: PDLCW04
- Pages: 151-162
- Type: Article (dropdown menu)
- Access / Copy: (empty field)
- Journal: Appl. Clay Sci. (dropdown menu)
- Volume: 26
- Comment: (empty text area)
- Internal Status: Pure Listing (dropdown menu)
- Last Modification at: 09.08.2004 15:42:00 (with a clock icon)
- by: anke

At the bottom of the form, there is a footer section with several icons: a printer, a question mark, a memo, a pencil, a warning sign, and a back arrow. Below the icons, it says "Datensatz: 1457 von 1461".

Fig. 15: Input and editing form for publication data (here: article in a journal)

The "Memo" button in the footer section of this form converts the bibliographic reference into formats according to editorial guidelines of different journals. The formatted reference is shown in a separate window, already marked and highlighted ready for

“Cut & Paste” into other documents. The desired journal style can be selected through the “Administration” menu, see there for details.

**Author(s):** Names are separated by commas, each family name is followed (after a space) by the surnames abbreviated to their first letter and with no space or punctuation between the surnames.

*Examples:* MacNaughton MG, Garcia-Delgado RA, Garcia-Herruzo F

**Title:** Title of the publication without any enclosing quotation marks.

**Year:** Year of the publication (Ph.D. thesis sometimes appear with year of delivery!).

**Mnemonic Code:** This field represents an abbreviated code (mnemonic acronym) for the bibliographic record. Each entry must be unique. It is constructed from the first letter of each of the up to five first authors followed by the two trailing numbers of the publication year and optionally a small letter to distinguish otherwise identical codes (starting with a).

*Examples:* CCE02, S87a, Tzsne99

**Pages:** First and last page of the publication connected with a hyphen. In case of books it is also possible to enter the number of pages directly followed by "pp".

*Examples:* 124-135, 346pp

**Type:** Type of the publication, select from a scroll list. This list is stored in the table “PaperType”. A direct editing in this table is, however, not recommended because several interface procedures use code specific to each paper type. Currently, the paper types already include Article, Book, Chapter in Book, Proceedings, Internal Report, Chapter in Report, Personal Communication, Ph.D. Thesis, M.Sc. Thesis, WWW link / URL, Patent, Norm / Standard. This should cover the vast majority of possible reference source types.

**Access / Copy:** Hard copy registration number for publications where a hard copy is available, otherwise information about where to look for that publication is stored there. For internal use only, this field may be deleted / hidden for external users in later revisions.

**Journal:** Title of the journal, select from a scroll list. This list is stored in the table "Journals" and can be edited there directly if necessary, there is no extra input mask available.

**Volume:** Volume of the journal. This field may also contain the number (registration code) of reports, then it is labeled **Report No.**

**Chapter:** Chapter of a book or report.

**URL:** WWW link to online publications, must be a valid URL and should start with "http://".

**Book:** Title of the book or report, including the subtitle and the edition number.

**ISBN:** International registration number for books, can be given with or without the usually used hyphens. This field can also contain the ISSN number for regularly issued series.

**Town:** Publishing place of the book.

**Publisher:** Publisher of the book (company or institution).

**Editor(s):** Editors of the book, the input style is the same as for the authors.

**Comment:** Further bibliographic information (e.g. Dissertation Abstracts No.), remarks about duplications and contradictions, wrong citations, missing values, missing references to original raw data sources, other publications citing that work, short summaries about content. Here it should also be noted if the paper actually contains no extractable information about SCM (could be the case in review articles or works covering theoretical aspects, model comparisons or structural investigations).

## **6.2 Mineral**

This form (Fig. 16) is used to edit all information required to characterize the minerals. See also under the chapter "Content Policy" for the definitions of a mineral phase.

Fig. 16: Input and editing form for mineral data

**Official English Name:** Correct mineralogical name of the mineral.

**Alternative / Trivial Name:** Trivial / commercial name of the mineral in English.

**Formula:** Chemical formula of the mineral. There are only few examples of minerals with alternative chemical formulae (namely ferrihydrite). The pragmatic approach used here is to specify just one formula, and recalculate accordingly all values based on the alternative formulae (which then of course must be mentioned in the comment field). This affects only site densities given in units of mol / mol solid, mol / mol metal ion, and mol / g metal ion.

**Mineral Group:** Select from a scroll list. The categories are based on the chemistry and structure of the minerals, namely the dominating anion. If a mineral group is not available it can be added directly in the table "MineralGroup" (there is no extra input mask available).

**Mineral Series:** Select from a scroll list. The categories are based on petrologic considerations. If a mineral series is not available it can be added directly in the table "MineralSeries" (there is no extra input mask available).

**Molar Mass:** Molar mass for the above given formula in mol / g.

**Density:** Mineral density in g / cm<sup>3</sup>, can be given as a range.

**Add / Edit Reactions:** The button will open an additional form "Mineral Alteration and Kinetics". There respective mineral reactions can be specified. This form is also accessible through the "Advanced Editing" menu. See there for further details.

**Comment:** Additional remarks such as further alternative formulae, modifications, occurrence, being a solid solution end-member etc.

### 6.3 Sample Specific Data

This form (Fig. 17) summarizes the information that characterizes the samples used in sorption experiments. This includes sample origin, preparation steps, and analytical results.

Fig. 17: Input and editing form for sample specific data

**Mineral:** Select from a scroll list. If not available, go back to the input mask "Mineral" and add the respective mineral. See there for further details.

**Original Publication:** Select from a scroll list, if not available, go back to the input mask "Publication" and add the respective paper. See there for further details.

**Citation in:** If information is only cited in a secondary data reference, add this citing paper. If later access to the original reference is available, clear the citation entry and move the information about citation(s) into the comment field.

**Primary Sample Origin:** Origin of the mineral phase (commercial, synthetic or natural product).

**Supplier:** Manufacturer of a commercial product or depository for a natural product. Select from a scroll list. If a supplier is not available it can be added directly in the table "Supplier" (there is no extra input mask available).

**Sample Name:** Name of a commercial product or a natural product from a depository. Select from a scroll list. If a sample name is not available it can be added in the table "SampleName" (there is no extra input mask available).

**Preparation:** Preparation / processing details including literature references.

**Area Size:** Input of the SSA (Specific Surface Area) in  $\text{m}^2 / \text{g}$  with its associated error.

**Experiment:** Method for the determination of SSA, select from a scroll list. If not available, go back to "Advanced Editing" and add the respective method under "Experimental Method". See there for details.

**Grain Size:** in  $\mu\text{m}$ , can also be a range or upper / lower limit (< / >).

**Comment:** Additional remarks such as details about the method of SSA determination (e.g.  $\text{N}_2$ - or Ar- or Kr-BET), uncertainty of SSA determination, comparison with reference data and with data of (un)treated samples, assessment of the value, analytical phase verifications, purity etc.

## **6.4 Site Density & Surface Protolysis**

This form (see Fig. 18) contains all data about the surface binding sites: their type, density (surface concentration) and protolysis constants.

**RES<sup>3</sup>T: Site Density & Surface Protolysis** PID: 745

Mineral: Quartz Original Publication: R82  
 Citation in:   
 Specific Surface Area: 4.15 m<sup>2</sup> / g PZC: 3  
 Ionic Strength: 0 mol / L of NaNO<sub>3</sub> Capacitances in F / m<sup>2</sup>  
 C1: 1.3 C2: 0.2  
 Solid/Liquid Ratio: g / L  
 SCM Type: Triple Layer  
 Fit Method: graphic extrapolation Add / Edit Site Data

*Site Specific Data*

Surface Site Density		Protolysis Constants	
Experimental Methods: Tritium Exchange		Potentiometric Titral	
Type:	in sites / nm <sup>2</sup> sur1	pK1:	pK2:
A	»Si-OH 4.5	-0.95	6.65
B			
C			

Comment: citation in [ZS94]: also other value for pK2: 6.8 [cited from [ZACS90)]; double extrapolation technique to ionic strength 0; same values for background electrolyte NaCl

Internal Status: Details Last Modification at 10.08.2004 10:26:40 by anke

Datensatz: 213 von 1050

Fig. 18: Input and editing form for site density and surface protolysis data

**Mineral:** Select from a scroll list, if not available, go back to the input mask "Mineral" and add the respective mineral. See there for further details.

**Original Publication:** Select from a scroll list, if not available, go back to the input mask "Publication" and add the respective paper. See there for further details.

**Citation in:** If information is only cited in a secondary data reference, add this citing paper. If later access to the original reference is available, clear the citation entry and move the information about citation(s) into the comment field.

**Specific Surface Area:** Reference to the used specific surface area (SSA), either the same work or taken from another publication. Select from a scroll list presenting the numerical value of SSA in m<sup>2</sup> / g and the publication reference code. The relation between surface site density (SSD) and SSA falls into one of two categories: A) The SSD was determined independent from a value of the SSA, e.g., by means of theoretical, crystallographic considerations. Then the user has later to specify an own SSA value in order to allow SSD conversions into other units. B) The SSD was determined together with a SSA value. Then this value and the respective literature reference must be given in the database.

**PZC:** pH of the point of zero charge (total charge of the surface is zero). Sometimes are other values are also given (should be noted in the comment field): the PZNPC (point of zero net proton charge: pH of the point where the surface charge caused by only proton and hydroxyl adsorption is zero), PZNC (point of zero net charge: pH of the point where the surface charge caused by adsorption of other ionic ligands is zero), IEP (isoelectric point, some authors use it as synonym for PZC), PPZC (pristine point of zero charge: pH at which the sum of negative and positive charge becomes zero)

**Ionic Strength ... of:** Ionic strength of the background electrolyte in mol / L. If experiments for various ionic strengths are reported, specify the lowest one in this field and mention the other ones in the comment field. If the reported protolysis constants refer to an extrapolated infinite dilution, leave the field blank and specify all experimental ionic strengths in the comment field. If there are mixed background electrolytes or experiments with different electrolytes, specify them in the comment field. The type of the background electrolyte / medium / salt can be selected from a scroll list. If not available, go directly to the table "Electrolyte" (there is no extra input mask available) and add the respective medium.

**Capacitances C1 and C2:** Input in F / m<sup>2</sup> (values given in other units should be converted before with a respective addition to the comment field below), depending on the SCM type one or both fields may stay empty. The capacitance C2 when required by the triple layer SCM but not specified should be set to the default value of 0.2 F / m<sup>2</sup>.

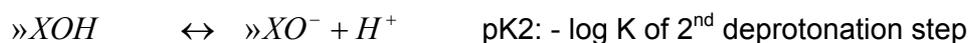
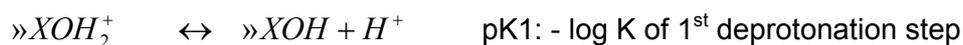
**Solid/Liquid Ratio:** Input in g/L (values given in other units should be converted before with a respective addition to the comment field below).

**SCM Type:** Select from a scroll list, if not available, go back to the "Advanced Editing" and add the respective model under "Surface Complexation Model". See there for details.

**Fit Method:** Method / software used to derive SCM parameters from the sorption experiment. Select from a scroll list. If a method is not available, go directly to the table "Fitting" (there is no extra input mask available) and add the respective method.

**Add / Edit Site Data:** The button will open an additional form "Site Specific Data". There site-type specific data for binding site densities and surface protolysis constants, accompanied by their respective uncertainties if available, can be specified. If a surface site type is not available yet for a certain mineral, one has to go to the "Advanced Editing" menu and assign this site type under "Surface Site Types" to the respective mineral. See there for details. The generic site types should only be used when it is not clear which site type is meant by the authors.

The surface protolysis constants for 2pK-models are defined as follows:



For an 1pK-model as (CD-)MUSIC only one protolysis constant is calculated, which should then be inserted in the pK1 field:



**Experimental Method:** Original data source for the derivation of surface site densities (SSD) and protolysis constants pK. This is not necessarily an experimental technique, but could also just be a value taken from the literature (from a single reference or as a weighted average), or be computed based on crystallographic data or other theoretical considerations. Select from a scroll list, if not available, go back to "Advanced Editing" and add the respective method under "Experimental Method". See there for details.

**In:** The unit for the surface site density values should always be the original one, an internal conversion to sites /nm<sup>2</sup> is already included in RES<sup>3</sup>T. If a site density unit is not available it can be added in the table "SiteUnit" (there is no extra input mask available). But then also the respective unit conversion routine must be added to the query "QProtolysis".

**Comment:** Additional remarks about the origin, quality, processing of data, or about other citations of the same data. This includes specification of ionic strength, source of values, other temperatures, validity of parameters, inconsistencies etc.

## 6.5 Surface Complex Formation

The form (see Fig. 19) manages the data records for all surface complex formation reactions. It is thus the core of the RES<sup>3</sup>T database.

Fig. 19: Input and editing form for surface complex formation

**Mineral:** Select from a scroll list, if not available, go back to the input mask "Mineral" and add the respective mineral. See there for further details.

**Original Publication:** Select from a scroll list, if not available, go back to the input mask "Publication" and add the respective paper. See there for further details.

**Citation in:** If information is only cited in a secondary data reference, add this citing paper. If later access to the original reference is available, clear the citation entry and move the information about citation(s) into the comment field.

**SCM Type:** Select from a scroll list, if not available, go back to "Advanced Editing" and add the respective model under "Surface Complexation Model". See there for details.

**Site Protolysis Reference:** Reference to the used site protolysis data, maybe the same work or citation from another publication, select from a scroll list presenting the publication reference code, the SCM type (acronym) being identical to the above selected SCM type, and the PID (unique protolysis data record identifier). The latter is important when a publication contains more than one different protolysis data sets for a given combination of mineral and SCM type.

**Ligands:** Selection of a major (1<sup>st</sup>, required) and secondary (2<sup>nd</sup>, for ternary surface complexes, optional) ligand forming the surface complex. In case of ternary complexes the metal should always become the 1<sup>st</sup> and an organic reaction partner become the

2<sup>nd</sup> ligand. If the required ligand is not available yet, go back to "Advanced Editing" and add the respective ligand under "Ligands". See there for details.

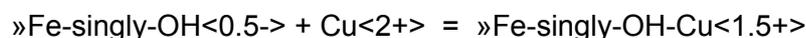
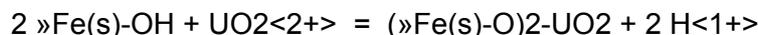
**Site Type:** Select from a scroll list. If a surface site type is not available yet for a certain mineral, one has to go to the "Advanced Editing" menu and assign this site type under "Surface Site Types" to the respective mineral. See there for details. Generic site types should only be used when it is not clear which site type is meant by the authors.

**Coefficients:** Specification of the stoichiometric coefficients for all components forming the surface complex. For reaction products, give negative numbers.

**Equation:** Equation of the chemical reaction forming the surface complex. The unreacted surface site always occurs on the left hand side.

**Proposal for Equation?:** The button will provide a proposal for the surface complex formation generated by the database. It can be accepted (the proposal will then automatically be inserted in the equation field) or rejected. To illustrate the notation recommended for chemical equations, some examples are given below. In case of ternary complexes the metal should always be written in front of an additional organic ligand.

*Examples:*



**log K ... ±:** Reaction constant for the surface complex formation. If published, the uncertainty of log K can also be included.

**Fit Method:** Method / software used to derive SCM parameters from the sorption experiment. Select from a scroll list. If a method is not available, go directly to the table "Fitting" (there is no extra input mask available) and add the respective method.

**Experiment:** Original data source for the derivation of surface complex formation constants. This is not necessarily an experimental technique, but could also be just taken from the literature (single reference or weighted average), or be computed based on crystallographic data or other theoretical considerations. Select from a scroll list, if not available, go back to "Advanced Editing" and add the respective method under "Experimental Method". See there for details.

**Ionic Strength ... of:** Ionic strength of the background electrolyte in mol / L. If experiments for various ionic strengths are reported, specify the lowest one in this field and mention the other ones in the comment field. If the reported protolysis constants refer to an extrapolated infinite dilution, leave the field blank and specify all experimental

ionic strengths in the comment field. If there are mixed background electrolytes or experiments with different electrolytes, specify them in the comment field. The type of the background electrolyte / medium / salt can be selected from a scroll list. If not available, go back to the table "Electrolyte" (there is no extra input mask available) and add the respective medium.

**Ligand is Itself Background Electrolyte:** Check this box if the above specified reaction concerns either anion or cation of the background electrolyte. This is only relevant for the triple layer and the 1pK SCM, therefore this check box is grayed out for all other SCM selections.

**Log K References for Electrolyte ... Anion ... Cation:** These two scroll lists only appear for triple layer and the 1pK SCM data records provided the check box for the background electrolyte is not checked. Here, the respective references to the background electrolyte reaction data can be selected. The lists comprise of the publication reference code, the already covered anions or cations, and the RID (unique reaction data record identifier). The latter is important when a publication contains more than one different background electrolyte reaction data set for a given combination of mineral and ion type. It is advisable to first put in the two records for the background electrolyte so that these entries are already available for selection when it comes to the other surface complexes.

**Comment:** Additional remarks about experimental details such as raw data reference code, ionic strength of background electrolyte if experiments for various ionic strength are reported, log K for other ionic strengths if values are not clearly assigned, citation of values in other references, formed complexes (mono-dentate, bi-dentate, inner sphere, outer sphere), note if the stored values are recalculated ones etc.

## 6.6 Advanced Editing

The menu "Advanced Editing" (see Fig. 20) combines input masks for all auxiliary information that usually is not changed very frequently.

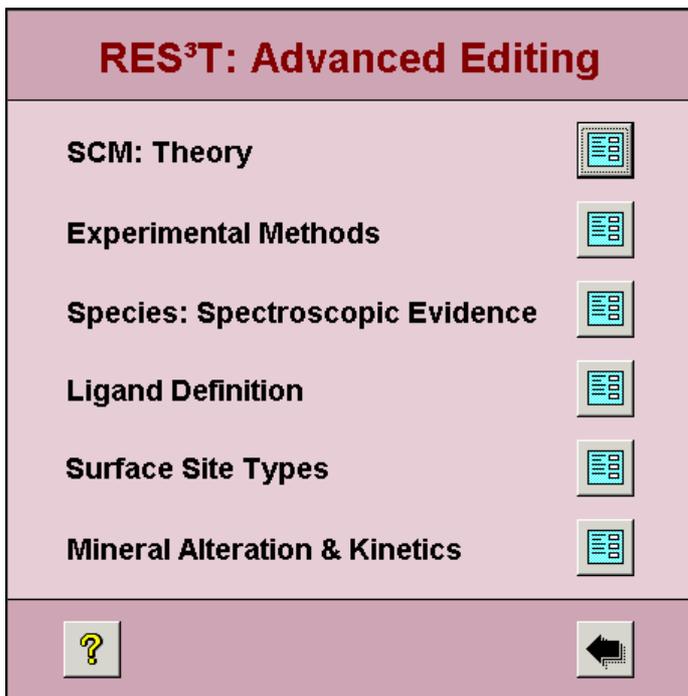


Fig. 20: Advanced Editing menu of the RES<sup>3</sup>T database

### 6.6.1 SCM: Theory

This menu (see Fig. 21) helps to maintain information about the various subtypes of surface complexation models in use. It should provide end users with some background knowledge about how to use and interpret SCM data.

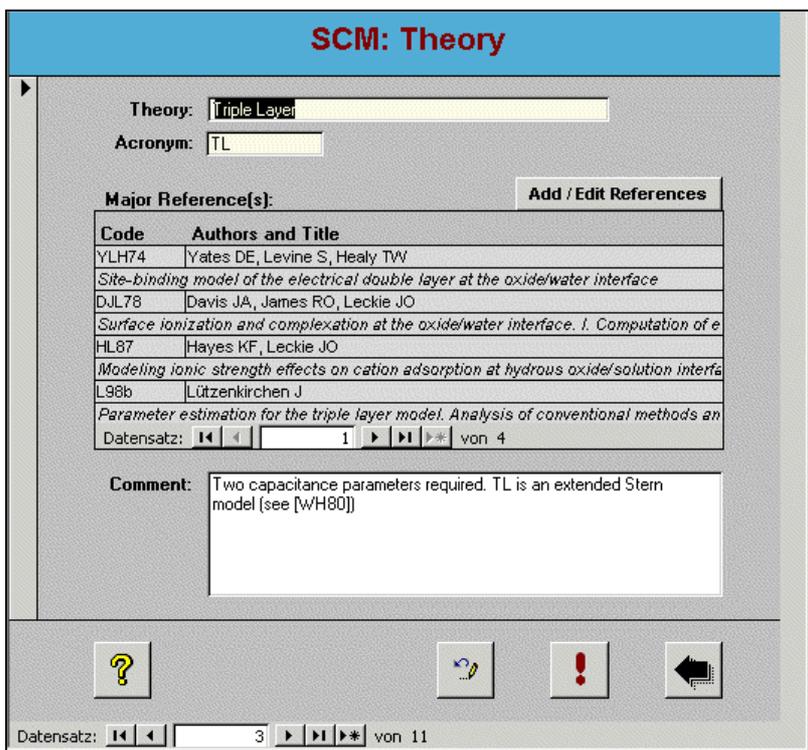


Fig. 21: Advanced Editing form for the SCM theory

**Theory:** Full name of the SCM sub-model / theory.

**Acronym:** Acronym of SCM sub-model / theory to be used in tables and scroll lists.

**Major Reference(s):** Important publications dealing with the SCM sub-model / theory, i.e. development of the theory, extensions, major applications, limitations etc. The table shows the literature reference code, authors, and title of the publications.

**Add / Edit References:** The button will open an additional form "Literature: SCM Theory" with the fields "SCM Type" (which defaults to the SCM type specified in the calling form), "Reference" (where a publication reference code can be selected from a scroll list), and "Comment" (a place for any additional remarks).

**Comment:** Additional remarks about theoretical aspects, application limits, required fit parameters, resemblances with other models, implicit assumptions about systems or parameters etc.

## 6.6.2 Experimental Methods

As for the SCM types above also this form (see Fig. 22) gives some short background information and essential references, but here with regard to experimental methods relevant for sorption experiments in a wider sense.

**Experimental Methods**

Technique: Potentiometric Titration

Major Reference(s): Add / Edit References

Code	Authors and Title
BM81	Balistrieri LS, Murray JW <i>The surface chemistry of goethite (α-FeOOH) in major ion seawater</i>
HS76	Hohl H, Stumm WV <i>Interaction of Pb<sup>2+</sup> with hydrous γ-Al<sub>2</sub>O<sub>3</sub></i>
KS80	Kummert R, Stumm WV <i>Surface complexation of organic acids on hydrous γ-Al<sub>2</sub>O<sub>3</sub></i>

Datensatz: 1 | von 3

Used to Derive ...

Specific Surface Area:	Surface Site Density:	Protolysis Constant:	log K Value:	Species Evidence:
<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>

Comment: often termed "acid-base-titration"

Datensatz: 2 | von 21

Fig. 22: Advanced Editing form for the experimental methods

**Technique:** Name of the experimental method

**Major Reference(s):** Important publications dealing with the experimental technique, i.e. development of the theory, extensions, major applications, limitations etc. The table shows the literature reference code, authors, and title of the publications.

**Add / Edit References:** The button will open an additional form "Literature: Experimental Methods" with the fields "Experiment" (which defaults to the experimental technique specified in the calling form), "Reference" (where a publication reference code can be selected from a scroll list), and "Comments" (a place for any additional remarks).

**Used to Derive ... :** Several check boxes indicating whether an experimental technique is suitable for the determination of specific surface areas, surface site densities, protolysis constants, complex formation constants, or for a proof of existence of a surface species.

**Comment:** Short description of the method and additional remarks about theoretical aspects, application limits etc.

### 6.6.3 Species: Spectroscopic Evidence

This menu offers a possibility to enter information about independent spectroscopic evidence for surface species. At present there are no data records provided, so it is up to the user to build his own database.

**Formula:** Chemical formula of the surface complex species

**Structure:** Proposed chemical structure model of the surface complex species as an image (e.g. scanned from a publication)

**Major Reference(s):** List of publications dealing with the proof of existence of the above surface complex species. The table shows the literature reference code, authors, title, and method dealt with for the publications.

**Add / Edit References:** The button will open an additional form "Literature: Species Evidence" with the fields "Species" (which defaults to the surface complex specified in the calling form), "Experiment" (where an experimental technique can be selected from a scroll list), "Reference" (where a publication reference code can be selected from a scroll list), and "Comments" (a place for any additional remarks).

**Comment:** Additional remarks.

## 6.6.4 Ligand Definition

This form (see Fig. 23) helps to define ligands (i.e. all complexants capable of sorbing to mineral surfaces, including not only contaminants but also matrix elements of any aqueous solution).

Element	Coefficient
O	2
U	1

Fig. 23: Advanced Editing form for the ligand definition

**Formula:** Chemical formula of the ligand with the charge appended enclosed in sharp brackets.

*Example:* UO2<2+> , Cl<1-> , bipy<0>

**Full Name:** Full name of the ligand

**Abbreviation:** Short form of the ligand name, e.g. in case of organic ligands such as NTA, EDTA etc.

**Oxidation State:** Only useful for ligands with central atoms / metals having uniform oxidation states. Not applicable to mixed redox compounds and most of the organic ligands.

**Charge:** Formal charge of the ligand according to the above specified formula

**Molar Mass:** Molar mass of the ligand in mol / g in the form as specified in the "Composition" table. This value is automatically computed and can not be edited.

**Radius:** Ionic or covalent radius of the ligand (not used so far)

**Composition:** Table for the chemical composition of the ligand, i.e. elements and their stoichiometric coefficients.

**Edit Stoichiometry:** The button will open an additional form "Composition of Ligands" with the fields "Ligand" (which defaults to the ligand specified in the calling form), "Element" (where a chemical element can be selected from a scroll list), and "Stoichiometric Coefficient" (where the respective stoichiometric coefficient must be entered).

### 6.6.5 Surface Site Types

This form (see Fig. 24) is used to define the relation between minerals and surface site types, i.e. which surface site types can be assigned to a mineral.

Site Types of Minerals		
Select Mineral:	Quartz	
Site Type:	»Si-OH	Stoichiometric Coefficient: 1
Site Type:	»Si(w)-OH	Stoichiometric Coefficient: 1
Site Type:	»Si(s)-OH	Stoichiometric Coefficient: 1
Site Type:	»Si-doubly	Stoichiometric Coefficient: 1
Site Type:	»Si-singly	Stoichiometric Coefficient: 1
Site Type:		Stoichiometric Coefficient: 1

Datensatz: 6 von 6 (Gefiltert)

Fig. 24: Advanced Editing form for the site types of minerals

**Mineral:** Select from scroll list. If the required mineral is not available yet, go to the input mask "Mineral" and add the respective mineral. See there for further details. Once a mineral is selected all site types associated so far to this mineral are listed.

**Site Type:** Select from a scroll list. Only entries relevant for the afore selected mineral are listed. The generic site types "»X-OH", "»X(w)-OH", "»X(s)-OH", and "»Y-OH" should only be used when it is not clear which site type is meant by the authors. Most often this happens when dealing with clay minerals and not distinguishing aluminol and silanol sites. If a required site type is not available yet, it has to be added directly to the table "SiteType", there is no separate input mask. Then the "Update" button of the "Site Types" form must be pushed to propagate the changes to this form.

**Coefficient:** Select from scroll list. The value gives the number of surface sites per formula unit of the mineral.

### 6.6.6 Mineral Alteration and Kinetics

This menu offers a possibility to enter information about chemical reactions forming, dissolving or altering minerals, including both thermodynamic and kinetic data. At present there are no data records provided, so it is up to the user to build his own database.

**Mineral Phases - Original:** Select from scroll list. Defaults to the mineral specified in the calling form.

**Mineral Phases - Product:** Select from scroll list. In case that there are two or more product minerals, select the more "complicated" one and put the others into the comment field.

**Chemical Reaction - Equation:** Equation formulated with the original mineral phase being on the left hand side and the product mineral phase(s) being on the right hand side.

**Chemical Reaction - log beta:** Reaction constant related to the above formulated equation.

**Chemical Reaction - Reference Code:** Publication reference code about the above chemical reaction, can be selected from a scroll list.

**Kinetic Rate Law - Equation:** Kinetic rate law for the above chemical equation in free format.

**Kinetic Rate Law - Parameters:** Values of up to three parameters of the above kinetic rate law.

**Kinetic Rate Law - Reference Code:** Publication reference code about the above kinetic rate law, can be selected from a scroll list.

**Comment:** Additional remarks.

## 7 Administration

This menu (see Fig. 25) combines several database management tasks, some of them being only accessible to users with administrator privileges. Respective buttons will be grayed out for other users.

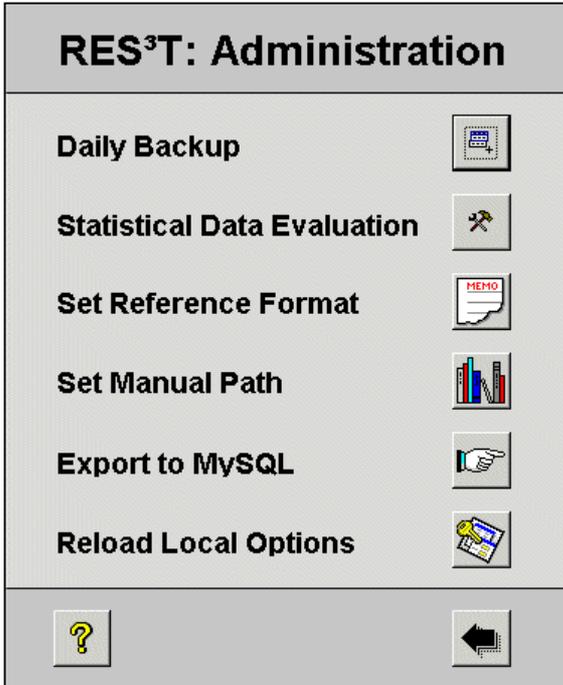


Fig. 25: Administration menu of the RES<sup>3</sup>T database

### 7.1 Daily Backup

Pressing this button starts a backup of all database tables into a new MS Access database. Its name follows the pattern "RES3T\_YMMMDD\_###.mdb", where YMMMDD stands for digits representing year, month and day of the backup, and ### stands for the current user name. The backup is placed in a directory specified by the "Local Option" setting "BackupPath". This button is not activated for users without administrative privileges.

### 7.2 Statistical Data Evaluation

This opens another menu with various options to perform a statistical data evaluation and to export the results into MS Excel spreadsheets to, e.g., create graphs or do more elaborate data processing. These spreadsheets will be placed in the directory specified under the entry "ExcelPath" of the "Local Options".

**Specific Surface Distribution:** Creates a table giving the number of SSA records per mineral, and puts the results into a spreadsheet named "SSA\_minerals.xls".

**Protolysis Data Distribution:** Creates a table giving the number of surface site protolysis records per mineral, and puts the results into a spreadsheet named "pk\_mineral.xls".

**log K Distribution:** Creates tables giving the number of surface complexation constants per SCM type, per ligand, per mineral and per mineral group. The results are put into spreadsheets named "logK\_SCM.xls", "logK\_ligand.xls", "logK\_mineral.xls", and "logK\_group.xls", respectively.

**Publication Statistics:** Creates tables giving the number of publications per year and per journal. The results are put into spreadsheets named "publ\_year.xls" and "publ\_journal.xls", respectively.

### **7.3 Set Reference Format**

Here you can preset the output format of the „Memo“ field in the publication input and editing form. Citation formats required by the editorial guidelines of the following journals can be selected:

- Geochimica et Cosmochimica Acta / Clays and Clay Minerals / Applied Geochemistry (**Default**)
- Journal of Colloid and Interface Science
- Environmental Science & Technology / Langmuir
- Soil Science Society of America Journal
- Colloids and Surfaces
- Radiochimica Acta
- Journal of Contaminant Hydrology

However, it must be pointed out, that the notation of the authors' names is not correct. Also italic and bold formats are not included.

### **7.4 Set Manual Path**

Here, the database administrator can specify whether the HTML-based online help should be accessed through the Internet or from a local file directory. This button is not activated for users without administrative privileges. The path required for Internet ac-

cess is predefined in the table "Administration" as entry "RES3T-URL" and must be a valid URL address. The local file directory can be set in the local options as entry "ManualPath". Either entries must not contain a trailing slash or backslash. The file name pointing to the correct HTML page is internally derived from the "StatusBarText" property of the "HelpButton" in all respective forms.

## **7.5 Export to MySQL**

Pressing the button "Export to MySQL" creates a script for use with the Open Source database MySQL. This script is named "esql\_add.txt" and is placed in the directory specified under the entry "MySQLPath" in the local options. The local options contain also the name of the MySQL database to be created, to be found under the entry "MySQLDatabaseName". The script "esql\_add.txt" is pure ASCII. It creates all required tables and fills them with the appropriate data records. It does, however, neither migrate the internal relationships between the tables, nor keep all the queries, forms, macros, and VBA modules used by MS Access. This button is not activated for users without administrative privileges.

The SQL export routine is designed to follow as close as possible the international SQL standard. As a result recently the RES<sup>3</sup>T database was also successfully converted into an Oracle 9i database.

## **7.6 Reload Local Options**

Pressing this button shows the current settings for several paths for programs or directories. They are required by RES<sup>3</sup>T but depend on the specific local PC installation RES<sup>3</sup>T is running on. These settings are read from a local initialization file and can be re-loaded through this menu button after any changes therein.

The options define various directories to store exported files in MS Excel format, MySQL format, or pure ASCII text. Here also the name of an exported MySQL file is specified, the path to a locally installed simple text editor (most often notepad.exe), and the path to the manual pages (either a local one or a WWW link address). Finally, the name of a path for backups of the RES<sup>3</sup>T tables is given. These settings are loaded at start from an initialization file named "res3t.ini" and placed in the local Windows system installation directory (most often C:\WIN, C:\WINNT, or C:\WINDOWS).

In case there is no initialization file available, the following default values will be loaded, with \$WINDIR\$ denoting the local Windows installation directory and \$TEMP\$ denoting the local temporary directory, both extracted automatically by RES<sup>3</sup>T from the respective system environment variables:

- ManualPath = "Manual"
- NotePad = \$WINDIR\$\notepad.exe
- BackupPath = \$TEMP\$\Backup
- ASCIIPath = \$TEMP\$\Export2ASCII
- ExcelPath = \$TEMP\$\Export2Excel
- MySQLPath = \$TEMP\$\Export2MySQL
- MySQLDatabaseName = "res3t"

Please ensure, that these directories, or the ones defined explicitly by the user in the initialization file, are really existing.

Whereas the path pointing to the manual must be relative to the place where the RES<sup>3</sup>T database itself is located, the paths for the export directories (ASCII, MySQL, and Excel) must be absolute ones including the hard disk drive letter.

## 8 General Help

Pressing the button “Help” will open the start page of an HTML-based RES<sup>3</sup>T manual, provided a web browser is already installed on the PC. Inside the manual one can navigate in the usual manner, with all the menu screenshots providing click-sensitive areas. In addition to this general help, most of the important menu forms also provide a help button in their footer section which will bring the user to a section of the online manual relevant for the respective menu form. The online manual essentially provides the same information as can be found in this document.

## 9 Acknowledgement

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