Computers & Geosciences 30 (2004) 959–967

COMPUTERS & GEOSCIENCES

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dSED: a database tool for modeling sediment early diagenesis[☆]

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Received 17 June 2003; received in revised form 3 May 2004; accepted 8 June 2004

Abstract

Mathematical modeling of sediment early diagenesis always involves choosing and describing a set of chemical reactions and processes that is both self-consistent and sufficient for the problem at hand. This critical choice is always a compromise between describing the system's complexity in all details and using a manageable set of reactions with known or obtainable parameters such as equilibrium and rate constants. We present a database tool for modeling sediment early diagenesis (dSED) that is designed to help modelers and sediment geochemists in this difficult conceptual step. The database should facilitate the development of state-of-the-art spatially continuous reaction-transport models (RTM), as well as simpler interacting-compartment (box) models. It allows one to explore: available kinetic and thermodynamic information, alternative descriptions of the same major processes, different degrees of completeness in description, processes and reactions that could be added or modeled differently, published solutions used by previous workers, and other information. The database is searchable and allows viewing reactions by specific products or reactants, types of processes, or other customized criteria. It operates under Microsoft Access™ and can be added to, modified and programmed by the user. The latest version of dSED and its user manual can be downloaded at http://www.science.uottawa.ca/LSSE/dSED.

Keywords: Reaction-transport modeling; Metal and nutrient cycling; Biogeochemical processes; Reaction kinetics; Online parameter repository

1. Introduction

Sediment early diagenesis reaction-transport models (RTMs) are based on complex and interconnected sets of chemical reactions and transport processes that describe spatially continuous dynamics of both solid and dissolved species in the sediment (e.g., Berner, 1980; Boudreau, 1997). They have been employed to model a broad range of aquatic environments, including marine (Boudreau, 1996; Klump and Martens, 1989; Dhakar and Burdige, 1996; Wang and Van Cappellen, 1996; Tromp et al., 1995), lacustrine (Furrer and Wehrli, 1996), estuarine (Regnier et al., 1997), ground water (Mayer et al., 2002; Hunter et al., 1998), and potentially other environments such as rivers and wetlands.

Sediment early diagenesis is, to a large degree, controlled by the kinetics of the involved biogeochemical and physical transformations. Whereas thermodynamic

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[☆] Data available from http://www.science.uottawa.ca/LSSE/dSED or from http://www.iamg.org/CGEditor/index.htm

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doi:10.1016/j.cageo.2004.06.005

equilibrium calculations have benefited from several good database/program combinations (e.g., Meeussen, 2003; Herberlin and Westall, 1999; Parkhurst and Appelo, 1999; Wolery, 1992a,b; Allison et al., 1991; Ball and Nordstrom, 1991), kinetic modeling of diagenesis is still in the early stages of a systematic integration of biogeochemical knowledge (Regnier et al., 2002a, b; Meysman et al., 2003a, b). At present, there exist no established database tools to classify and analyse the kinetic data that is essential to the development of sediment diagenesis RTMs.

An expandable web-distributed Knowledge Base (KB) (Regnier et al., 2002a, b, 2003) has recently been introduced to amend this situation. It is an ambitious attempt to synthesize and organize conceptual and quantitative biogeochemical information relevant to diagenetic modeling. The KB is currently designed to be integrated with a reaction-transport modeling software that is being developed by the same group at Utrecht University. A user of such software will choose from a collection of reaction pathways, rate law formulations and parameter values for a particular site or problem, or will have an option of accepting the proposed default values. The MEDIA code (Meysman et al., 2003a, b) is another recently developed software tool that is based on object-oriented programming concepts. Its object database was designed to facilitate adding reactions, species, and parameters (objects) to the associated MEDIA modeling software. The database is a library of ASCII files that contain descriptions of reactions, species, and parameters in a pre-defined format and that can be selected by the user in constructing a model. Both MEDIA and the KB significantly facilitate integration of the required biogeochemical knowledge into diagenetic modeling and will increase the universality of RTMs. At the same time, we feel that there is a further need for a more general database tool (and at this stage more complete) that is free from restrictions imposed by integration with simulation software.

In this paper, we present our "database for reaction-transport modeling of sediment early diagenesis", (dSED). It characterizes a diverse range of coupled biocatalytic, mineralogical, rheological, biological, photochemical, and other processes. Being complementary to KB and sharing much of its philosophy, our stand-alone tool offers flexibility provided by customizable search filters. Its main features, in comparison to those of KB and MEDIA, are presented in Table 1. dSED alleviates the historical bias in the data, as the database content is not selected based on subjective quality criteria or software formatting requirements. dSED can be used alone or in parallel with MEDIA or KB. Unlike KB, dSED does not provide in-depth reviews of current approaches, nor does it propose default parameter values and process formulations. dSED can also be used in parallel with equilibrium reaction databases, as we did not intend to include all available equilibrium data or all known aquatic speciation reactions. The database can also serve as a bibliographic tool.

Table 1
Comparison between diagenetic modeling databases

	dSED	KB	MEDIA
Implementation	MS Access™	Web	ASCII
Number of reactions[a]	199	24[b]	84
Online access	Yes	Yes	Yes
Integration with simulation software	No	Yes	Yes
Fixed data format	No	Yes	Yes
Data can be modified by user	Yes	No	Yes
New data can be added by user	Yes	Yes	Yes
Expert system	No	Yes	No
Data screened	No	Yes	Yes
Search capability	Yes	No	No
User-defined queries	Yes	No	No
Ability to retrieve published reaction sets	Yes	No	No
User-designed presentation format	Yes	No	No

[a] At the time of submission of this article.

[b] corresponds to the number of reactions and categories of reactions available online.

As the field of diagenetic reaction-transport modeling is itself relatively new (Steefel and Van Cappellen, 1998), dSED is intended to be a work in progress that interested workers can contribute to. We feel that this searchable collection of experimental and conceptual data will facilitate the development of both spatially continuous RTMs and simpler (e.g., box-type or interacting compartment) models. It will also benefit sediment geochemists who are concerned with interpretations of molecular and larger scale processes without necessarily performing model simulations. The database and its user manual are freely available on the Web at http://www.science.uottawa.ca/LSSE/dSED

Note that, in this paper, we use the term 'reaction' to include all processes that can be represented by a chemical reaction equation (including precipitation, dissolution, sorption, and surface complexation).

2. dSED motivation and philosophy

The philosophy, goals and possible uses of dSED have been elaborated with the potential for future development in mind and can be summarized as follows.

The database should include as many reactions and processes as possible. In contrast to expert systems like KB, dSED strives to include not only a "most important set" of established reactions and processes but also all those that *may* be relevant in aquatic environments, including those that have not yet been formulated for modeling in the form of chemical equations (e.g., Sinninghe Damsté et al., 1989). This is important because, for many systems, relevant chemical reactions and physical processes themselves have not always been identified or correctly represented. Non-discriminate inclusion of reactions ensures that the database is not biased to a particular model representation of diagenesis or school of thought. Instead, it allows exploring wide arrays of alternative descriptions and their consequences and permits identifying previously neglected but potentially important reactions.

As an example, no published RTM seems to consider manganese oxide reduction by dissolved ammonia

$$2NH_3 + 3MnO_2 + 6H^+ \rightarrow 3Mn^{2+} + N_2 + 6H_2O, \qquad (1)$$

whereas this reaction was suggested by Luther et al. (1997) to provide coupling between the diagenetic cycles of manganese and nitrogen and to offer an N_2 formation pathway alternative to the nitrification–denitrification cycle. The reaction is thermodynamically favorable (i.e., it reduces Gibbs free energy) at pH from 1 to 14. The rate of this reaction in natural sediments is, however, unknown.

Exploring alternative model formulations addresses the problem of non-uniqueness and non-completeness that is inherent to virtually all model reaction sets. Reaction sets that are either superficially different (e.g., contain alternative representations of the same processes) or fundamentally different (e.g., differ in the choice of processes) can produce the same degree of agreement with field observations. dSED should make it easier to evaluate the extent to which adding or removing reactions or processes (and/or changing parameters within their typical variability ranges) affects the model outputs.

dSED strives to characterize the reactions with as much kinetic and descriptive data as possible. Reaction rates and rate constants are particularly important. Finding correct values for reaction-specific kinetic parameters is a challenging task in RTM development because experimentally obtained values reported in the literature are often specific to particular field sites or to special natural or synthetic environmental conditions. Many reaction control parameters depend strongly on factors such as pH, Eh, ionic strength, salinity, temperature, or concentrations of solutes. In addition, experimental and field measurements often produce only the net rates for an assumed overall sequence of chemical reactions. Collecting and organizing all available data will help modelers in choosing the right parameters and will become a step towards developing generalized expressions to describe the control parameter dependencies on environmental conditions.

As an example, Wang and Van Cappellen (1996) obtained the rates of the reductive dissolution and precipitation of iron monosulfide

$$FeS + 2CO_2 + 2H_2O \leftrightarrow Fe^{2+} + 2HCO_3^- + H_2S \qquad (2)$$

by fitting their model's results to observations. Since this reaction is important to the diagenesis of iron, our database will benefit future models by providing the rate obtained by such model-fitting along with the rates experimentally measured under specific conditions (Morse et al., 1987; Rickard, 1995).

dSED should also help identify parameters whose values most need to be measured in order to constrain the available models. In that, the database will become a vehicle by which models can guide experimental studies.

Given that the same fundamental kinetic information (related to elementary chemical steps in an overall process) can often be applied to different aquatic environments, dSED can help transmit useful data across the different scientific communities that primarily deal with groundwater (Mayer et al., 2002; Appelo and Postma, 1993; Wolery, 1992a, b), surface water (Johnson et al., 1991; Shaffer, 1989; Imboden and Schwarzenbach, 1985), freshwater sediments (Roden and Wetzel, 2002; Furrer and Wehrli, 1996; Wersin et al., 1991), and marine sediments (Regnier et al., 2002a; Wang and Van Cappellen, 1996).

We put the kinetic data into a reaction-specific framework rather than sort it by the type of environment for which it was obtained. While knowing the latter is helpful to a modeler (and the environment type is specified for the database data whenever possible), reaction description in terms of geochemical control factors is more fundamental. Improved knowledge of reaction-specific parameters will make RTMs more adaptable to different field sites and environments.

3. dSED description: content

dSED contains the following types of information:

1. Reactions, including aqueous chemical reactions, solid phase precipitation and dissolution, and sorption. The reactions are characterized by their stoichiometries and by thermodynamic (Gibbs free energy change or equilibrium constant) and kinetic (rate law, rate constant) parameters. Sorption substrates are characterized by their surface properties. Parameters are given in the format and in the units of the original research articles and it is the responsibility of the database user to consult the original papers when using the parameters.
2. Transport mechanisms that act on and in the solid and liquid sediment fractions. Transport processes

include: diffusion, advection, bioturbation, bioirrigation, convection, including convection induced by in-situ gas bubble formation, sediment compaction, mixing due to wind and wave disturbances, and a water flow-induced mixing (dispersion). Typical rates, conditions, and the most common modeling approximations are described.

3. Information about whether a particular reaction was used in a published diagenetic model.

4. Bibliography. All information is fully referenced and a complete citation list is contained in a separate database table.

5. Standard reference data. In addition to the information specific to sediment diagenesis, the database contains some acid–base reactions and their dissociation constants, and electron potential changes in redox half-reactions. Many possible equilibrium aquatic speciation reactions are not included in dSED but can be easily identified by using geochemical equilibrium reaction databases (e.g., Meeussen, 2003; Herberlin and Westall, 1999; Parkhurst and Appelo, 1999). An extensive list of minerals and amorphous solid phases that may be important in sediment diagenesis is included in a separate database table and some of their properties are described.

The dSED list of substances that participate in sediment diagenesis reactions includes but is not limited to the following. Solid phases presently include: organic matter (represented by several typical compositions and organic compounds, on a continuum of average carbon redox states), oxides and oxyhydroxides of iron, manganese, and aluminum; sulfides and sulfates; calcium-, iron-, and manganese-bearing carbonates; phosphorus-bearing minerals (e.g., vivianite, hydroxyapatite), and silicates (e.g., biotite, chlorite). Aqueous species presently include: dissociated species of dissolved carbon dioxide, hydrogen sulfide, nitrogen compounds (ammonia and nitrates), phosphate, and iodine; oxygen, methane, sulfate, some intermediate organic compounds (e.g., acetic acid); dissolved species of iron, manganese, aluminum, calcium, and other metals and trace elements (e.g., As). Adsorption of dissolved ionic species is considered on a number of substrates including: particulate organic matter, bacterial cell walls, and the surfaces of minerals and amorphous materials. The latter include: iron-bearing (e.g., hematite, magnetite, oxyhydroxides) and manganese-bearing (e.g., rhodocrosite) solid phases, aluminum oxyhydroxides, calcium carbonates, and clays.

Table 2 summarizes the current scope and size of dSED. Table 3 gives an example of the types of reactions included by listing reactions that involve manganese. It should be emphasized that the reaction list in Table 3 reflects a work in progress and is not a complete description of manganese diagenesis.

Table 2
dSED database summary[a]

General information	
Total number of reactions	199
References cited	247
Minerals listed	330
Adsorption substrates	18
Transport processes	8
Models referenced	39
Reactions by reactive species	
Reactions involving Al (all species)	15
Reactions involving As (all species)	16
Reactions involving Fe (all species)	81
Reactions involving Mn (all species)	28
Reactions involving N (all species)	33
Reactions involving P (all species)	18
Reactions involving CH_4	13
Reactions involving $Fe(OH)_3$	36
Reactions involving FeS	22
Reactions involving FeS_2	19
Reactions involving H_2S	33
Reactions involving MnO_2	18
Reactions involving NO_3^-	21
Reactions involving NH_4^+	17
Reactions involving SO_4^{2-}	49
Reactions involving organic matter	33
Reactions by reaction type	
Biocatalyzed reactions	68
Inorganic reactions	69
Precipitation/dissolution reactions	89
Photochemical reactions	6
Redox reactions	119

[a] At the time of submission of this article.

4. dSED description: implementation

The database is implemented in Microsoft Access™, an easily available database software. The main entries in the database are individual reactions. For each reaction, the corresponding database record contains the reaction equation and, in many cases, its alternative forms (that is, reactions differing in the stoichiometries of their reactants, the ionic speciation, or the mineral species). The database also provides a short descriptive name of the reaction, values of thermodynamic parameters, reaction rates, rate laws and rate constants, descriptions of its typical effects on the system's pH and Eh, catalyst information, and bibliographic references. Where possible, the reactions are listed in the forms that are most commonly used in modeling. (Alternative reaction forms are not necessarily equivalent among themselves as they may differ, for example, in their effect on the system's pH.) Comments provide information about the typical geochemical environments in which a

Table 3
List of dSED reactions involving manganese[a]

	Reaction
1	$CH_2O+2\ MnO_2(s)+3\ CO_2+H_2O=2\ Mn^{2+}+4\ HCO_3^-$
2	$2\ Fe^{2+}+MnO_2\ (s)+4\ H_2O=2\ Fe(OH)_3(s)+Mn^{2+}+2\ H^+$
3	$4\ MnO_2(s)+FeS(s)+8\ H^+=4\ Mn^{2+}+SO_4^{2-}+Fe^{2+}+4\ H_2O$
4	$2\ Mn^{2+}+O_2+2\ H_2O=2\ MnO_2\ (s)+4\ H^+$
5	$4\ MnO_2\ (s)+NH_4^++6\ H^+=4\ Mn^{2+}+NO_3^-+5\ H_2O$
6	$3\ MnO_2\ (s)+2\ NH_4^++4\ H^+=3\ Mn^{2+}+N_2+6\ H_2O$
7	$MnO_2\ (s)+HS^-+3\ H^+=Mn^{2+}+S^0+2\ H_2O$
8	$x\ Mn^{2+}+(1-x)\ Ca^{2+}+2\ HCO_3^-=Mn_xCa_{(1-x)}CO_3(s)+CO_2+H_2O$
9	$Mn^{2+}+2\ HCO_3^-=MnCO_3\ (s)+CO_2+H_2O$
10	$S–Mn^++1/2\ O_2+HCO_3^-=S–H^0+MnO_2\ (s)+CO_2$
11	$S–H^0+Mn^{2+}+HCO_3^-=S–Mn^++CO_2+H_2O$
12	$5Mn^{2+}+2\ NO_3^-+4\ H_2O=5\ MnO_2\ (s)+N_2+8\ H^+$
13	$3\ Mn^{2+}+IO_3^-+3\ H_2O=3\ MnO_2\ (s)+I^-+H^+$
14	$2\ NH_3+3\ MnO_2\ (s)+6\ H^+=3\ Mn^{2+}+N_2+6\ H_2O$
15	$NH_3+4\ MnO_2\ (s)+7\ H^+=4\ Mn^{2+}+NO_3^-+5\ H_2O$
16	$4\ Mn^{2+}+8\ OH^-+O_2=4\ MnOOH\ (s)+2\ H_2O$
17	$FeS_2\ (s)+7.5\ MnO_2\ (s)+11\ H^+=Fe(OH)_3\ (s)+2\ SO_4^{2-}+7.5\ Mn^{2+}+4\ H_2O$
18	$6\ Mn^{2+}+IO_3^-+9\ H_2O=MnOOH\ (s)+I^-+2\ H^+$
19	$MnO_2\ (s)+2\ I^-+4\ H^+=Mn^{2+}+I_2+2\ H_2O$
20	$6\ MnOOH\ (s)+2\ NH_4^++10\ H^+=6\ Mn^{2+}+N_2+12\ H_2O$
21	$8\ MnOOH\ (s)+NH_4^++14\ H_+=8\ Mn^{2+}+NO_3^-+13\ H_2O$
22	$2\ MnCO_3\ (s)+O_2+2\ H_2O=2\ MnO_2\ (s)+2\ HCO_3^-+2\ H^+$
23	$Mn^{2+}+HS^-=MnS\ (s)+H^+$
24	$3\ Mn^{2+}+2\ PO_4^{3-}+3\ H_2O=Mn_3(PO_4)2\cdot 3H_2O\ (s)$
25	$MnO_2\ (s)+4\ H^++2\ Fe^{2+}=Mn^{2+}+2\ H_2O+2\ Fe^{3+}$
26	$Mn(OH)_2=MnOH^++OH^-$
27	$H_3AsO_3+MnO_2\ (s)+H^+=H_2AsO_4^-+Mn^{2+}+H_2O$
28	$H_2+MnO_2\ (s)+2\ H^+=Mn^{2+}+2\ H_2O$

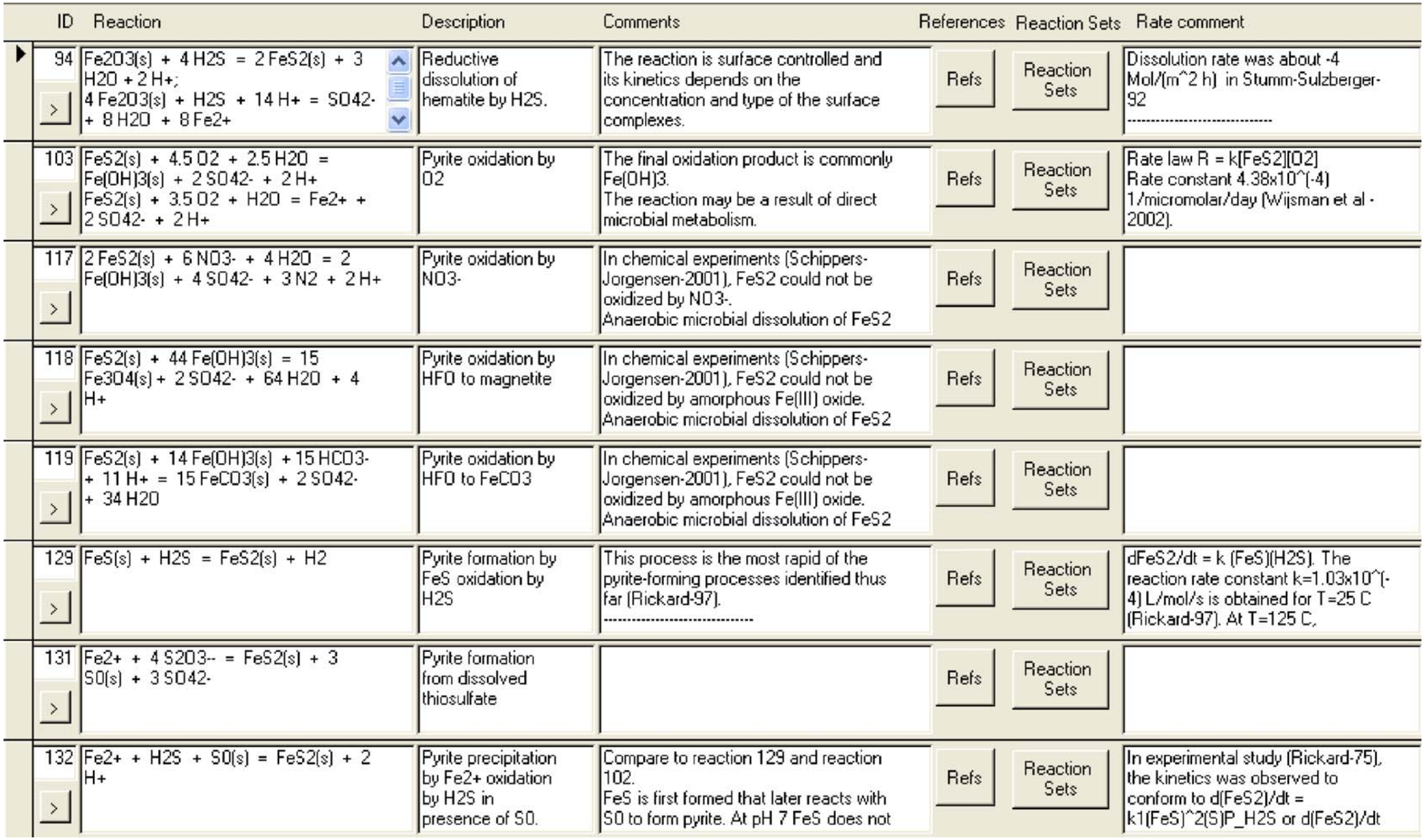
S-denotes a surface complex.

[a] Alternative reaction formulations (for different acid–base speciations, reactant stoichiometries, or mineral species) are not shown.

Table 4
Presently available dSED forms

Form name	What it displays
Main forms	
All reactions	All reactions in the database
Adsorption	Adsorption properties for various combinations of species and substrates
Electron half-reactions	Redox reactions in their electron half-reaction representations
New reaction entry	Data for one reaction at a time, in a large window
Minerals	A list of sediment mineral and amorphous solid phases
Transport processes	Descriptions of transport processes in sediments
Reference data forms	
Abbreviations and symbols	Abbreviations used in the database
General comments	Miscellaneous comments on the database use
Acid–base reactions	A reference list of acid–base reactions
Electron half-reaction list	Elementary electron half-reactions
Adsorption substrates	A list of substrates and their properties with respect to adsorption
Mineral classes	A list of mineral classes and their brief descriptions
Models	Names of models with citation information and short descriptions
Literature	Bibliographic references
Reactions by type	Reactions of a specific type (see Table 2)
Reactions by species	Reactions involving a specified species as one of the reactants or products (see Table 2)

Table 5
Partial dSED response to a query about reactions involving pyrite[a]



ID	Reaction	Description	Comments	References	Reaction Sets	Rate comment
94	Fe2O3(s) + 4 H2S = 2 FeS2(s) + 3 H2O + 2 H+; 4 Fe2O3(s) + H2S + 14 H+ = SO42- + 8 H2O + 8 Fe2+	Reductive dissolution of hematite by H2S.	The reaction is surface controlled and its kinetics depends on the concentration and type of the surface complexes.	Refs	Reaction Sets	Dissolution rate was about -4 Mol/(m^2 h) in Stumm-Sulzberger-92 ------------------------------
103	FeS2(s) + 4.5 O2 + 2.5 H2O = Fe(OH)3(s) + 2 SO42- + 2 H+ FeS2(s) + 3.5 O2 + H2O = Fe2+ + 2 SO42- + 2 H+	Pyrite oxidation by O2	The final oxidation product is commonly Fe(OH)3. The reaction may be a result of direct microbial metabolism.	Refs	Reaction Sets	Rate law R = k[FeS2][O2] Rate constant 4.38x10^(-4) 1/micromolar/day (Wijsman et al - 2002).
117	2 FeS2(s) + 6 NO3- + 4 H2O = 2 Fe(OH)3(s) + 4 SO42- + 3 N2 + 2 H+	Pyrite oxidation by NO3-	In chemical experiments (Schippers-Jorgensen-2001), FeS2 could not be oxidized by NO3-. Anaerobic microbial dissolution of FeS2	Refs	Reaction Sets	
118	FeS2(s) + 44 Fe(OH)3(s) = 15 Fe3O4(s) + 2 SO42- + 64 H2O + 4 H+	Pyrite oxidation by HFO to magnetite	In chemical experiments (Schippers-Jorgensen-2001), FeS2 could not be oxidized by amorphous Fe(III) oxide. Anaerobic microbial dissolution of FeS2	Refs	Reaction Sets	
119	FeS2(s) + 14 Fe(OH)3(s) + 15 HCO3- + 11 H+ = 15 FeCO3(s) + 2 SO42- + 34 H2O	Pyrite oxidation by HFO to FeCO3	In chemical experiments (Schippers-Jorgensen-2001), FeS2 could not be oxidized by amorphous Fe(III) oxide. Anaerobic microbial dissolution of FeS2	Refs	Reaction Sets	
129	FeS(s) + H2S = FeS2(s) + H2	Pyrite formation by FeS oxidation by H2S	This process is the most rapid of the pyrite-forming processes identified thus far (Rickard-97). ------------------------------	Refs	Reaction Sets	dFeS2/dt = k (FeS)(H2S). The reaction rate constant k=1.03x10^(-4) L/mol/s is obtained for T=25 C (Rickard-97). At T=125 C,
131	Fe2+ + 4 S2O3-- = FeS2(s) + 3 S0(s) + 3 SO42-	Pyrite formation from dissolved thiosulfate		Refs	Reaction Sets	
132	Fe2+ + H2S + S0(s) = FeS2(s) + 2 H+	Pyrite precipitation by Fe2+ oxidation by H2S in presence of S0.	Compare to reaction 129 and reaction 102. FeS is first formed that later reacts with S0 to form pyrite. At pH 7 FeS does not	Refs	Reaction Sets	In experimental study (Rickard-75), the kinetics was observed to conform to d(FeS2)/dt = k1(FeS)^2(S)P_H2S or d(FeS2)/dt

[a] For brevity, only selected fields are shown and the display is limited to four lines per field.

particular reaction occurs, whether it is multistep, microbially mediated, and so on. Comments also detail the conditions in which empirically determined parameters were obtained, the significance of a particular reaction in sediment diagenesis in various environments, and other data. A separate comment field is provided for the kinetics-related information, to better describe the conditions in which the reaction rates were measured, the functional form of the reaction rate laws, and the specifics of the reaction kinetics in different environments. Redox reactions are also presented in a half-reaction form, which emphasizes the effect of those reactions on a system's Eh. A separate Reaction Set field indicates whether a particular reaction was part of a reaction set in some published model, in which case a bibliographic reference is provided. It can be used for extracting complete published reaction sets, comparing them, and performing gap analysis for missing reactions or species.

For a number of chemically similar substances, the corresponding reactions are often written for only one of those substances. For example, reactions that involve ferrihydrite (described by nominal composition $Fe(OH)_3$ and often referred to as hydrous ferric oxide) as one of the reactants or products can also describe some reactions involving goethite (α-FeOOH), provided that the reaction stoichiometries are adjusted accordingly. However, such substitutions should be used with caution because these minerals differ substantially in their properties, for example, in solubility (Wersin et al., 1991), and because the exact mineral phases are not always correctly identified in the experiments in which kinetic or other reaction parameters are obtained (e.g., Van der Zee et al., 2003).

Database information can be retrieved by using a number of Microsoft Access™ Forms (see dSED user manual (Katsev et al., 2003) and Table 4). Forms allow viewing all database reactions in a single table or selectively extracting information according to some selection criteria. For example, a researcher interested in the diagenetic cycling of iron can retrieve all reactions that involve Fe or a particular Fe-bearing compound as a reactant or product. Table 5 shows a partial list of reactions retrieved by querying dSED for the reactions involving pyrite (FeS_2) (some information was excluded from the presentation, for clarity). The first (leftmost) field contains the reaction identification number (ID), which is a unique number by which the reactions are referenced in the database. A button [>] located under each ID field posts the information for the selected reaction in a separate, larger, database window for better viewing. Empty Rate Comments fields indicate that the corresponding reaction rate information has not yet been found in the diagenetic literature reviewed to-date.

As a further example, Table 6 shows the result of database filtering for the reactions involving arsenic, which is an important toxic trace metal (Smedley and Kinniburgh, 2002). Reaction 16 (Table 6) of As coprecipitation with ferrihydrite was described only recently (Rancourt et.al., 2001). Given the biogeochemical similarity between As and P, more As reactions can be discerned using the selection of dSED reactions involving P.

A user familiar with basic principles of programming in Access™ can easily expand the list of available Forms and filters (Table 4) to customize the database for the problem at hand. More detailed information about the

Table 6
A list of dSED reactions involving arsenic

	Reaction
1	$As_4O_6 + 6\ H_2O = 4\ H_3AsO_3$
2	$As_4O_6 + 6\ H_2O = 4\ H_3AsO_3$
3	$As_2S_3 + 6\ H_2O = 2\ H_3AsO_3 + 3\ HS^- + 3\ H^+$
4	$As_2O_5 + 3\ H_2O = 2\ H_3AsO_4$
5	$Ca_3(AsO_4)_2 \cdot 6H_2O + 6\ H^+ = 2\ H_3AsO_4 + 3\ Ca^{2+} + 6\ H_2O$
6	$Fe_3AsO_4 \cdot 2H_2O + 3\ H+ = H_3AsO_4 + Fe^{3+} + 2\ H_2O$
7	$AsS + 3\ H_2O = H_3AsO_3 + HS^- + 2\ H^+ + e^-$
8	$CH_2O + 2\ H_2AsO_4^- + H^+ = HCO_3^- + 2\ H_3AsO_3$
9	$H_3AsO_3 + 0.5\ O_2 = H_2AsO_4^- + H^+$
10	$H_3AsO_3 + 0.4\ NO_3^- = H_2AsO_4^- + 0.2\ N_2 + 0.2\ H_2O + 0.6\ H^+$
11	$H_3AsO_3 + MnO_2 + H^+ = H_2AsO_4^- + Mn^{2+} + H_2O$
12	$4\ H_2AsO_4^- + HS^- + 3\ H^+ = 4\ H_3AsO_3 + SO_4^{2-}$
13	$3\ H_2AsO_4^- + S^0 + H^+ + H_2O = H_3AsO_3 + SO_4^{2-}$
14	$4\ H_2AsO_4^- + FeS + 4\ H^+ = 4\ H_3AsO_3 + SO_4^{2-} + Fe^{2+}$
15	$7\ H_2AsO_4^- + FeS_2 + 5\ H^+ + H_2O = 7\ H_3AsO_3 + 2\ SO_4^{2-} + Fe^{2+}$
16	$Fe^{3+} + y\ AsO_4^{3-} + (x + 2\text{-}2y)\ H_2O = Fe[(OOH)_{1-x-y}(OH)_{3x}(AsO_4)_y] + (3\text{-}3y)\ H^+$

programming aspects of dSED can be found in the dSED user manual (Katsev et al., 2003). The manual also contains references to bibliographic and online resources relevant to sediment early diagenesis modeling.

5. Summary

dSED is a valuable database tool for RTM, box-model, and interpretation development in sediment early diagenesis. We invite all interested researchers to contribute to it with experimental, theoretical, or bibliographic data. The dSED database is maintained by the Lake Sediment Structure and Evolution (LSSE) group at the University of Ottawa. Contributions to the database can be made by e-mail to the corresponding author.

Acknowledgements

The authors would like to thank Frederick Ghogomu, Darryl Roberts and Claar van der Zee for their helpful suggestions and Filip Meysman and an anonymous reviewer for constructive criticism. This work was funded by a Strategic Project Grant from the Natural Sciences and Engineering Research Council of Canada.

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