The PSI/Nagra Chemical Thermodynamic Database 12/07: Present status and future developments

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The PSI/Nagra TDB has been updated from version 01/01 [1] to version 12/07 to support the ongoing safety assessments for a deep underground repository for radioactive waste in Switzerland. TDB 12/07 contains three types of data: (1) Core data are widely accepted data of high-quality that are mainly based on the CODATA key values. (2) Recommended data are also of high quality, but they originate from rather active fields in the environmental sciences and may be revised over time. They are mainly based on the critical reviews of data for U, Am, Tc, Np, Pu, Ni, Se, Zr, and Th provided by NEA in their "Chemical Thermodynamics" series. (3) Supplemental data are suitable for scoping calculations. Some estimates are made in cases where their omission would lead to obviously erroneous results. TDB 12/07 is provided for use with the geochemical modeling codes GEMS [2] and PHREEQC [3].

Further development of the database will run along the following lines: (1) Data for Sn will be included from the latest NEA review [4] and for Fe and Mo from forthcoming NEA reviews, as well as data from the IUPAC reviews, e.g. [5], on the chemical speciation of environmentally significant metals (at present Hg, Cu, Pb, and Cd). (2) Since a large part of the data included in TDB 12/07 is applicable only at 25°C, estimation methods [6] have to be considered for extending the application range to the higher temperatures expected in the repository environment. (3) Experimental data were reduced to zero ionic strength by NEA and IUPAC using the specific ion interaction theory SIT [6]. SIT coefficients are not known for many aqueous species (especially in NaCl background media). In order to use the SIT in geochemical modeling of natural systems, estimation methods have to be found to fill these gaps.

[1] Hummel *et al.* (2002) Nagra/PSI Chemical Thermodynamic Data Base 01/01. Nagra NTB 02-16. Nagra, Wettingen, Switzerland. [2] Kulik *et al.* (2013) *Min. Mag.* (this volume). [3] Parkhurst *et al.* (1999) Water-Resources Investigations Report 99-4259, Denver. [4] Gamsjäger *et al.* (2012) Chemical Thermodynamics of Tin. OECD Publications, Paris. [5] Powell *et al.* (2011) *Pure Appl. Chem.* **83**, 1163-1214. [6] Grenthe *et al.* (eds.) (1997) Modelling in Aquatic Systems. OECD Publications, Paris.

Biogeochemical cycling of nitrogen on the early Earth

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There has been considerable recent interest in variations of the nitrogen isotope composition of ancient organic matter and associated sediments as they provide clues for the early evolution of Earth's atmosphere-ocean-biosphere system. In particular, large $\delta^{15}N$ isotopic variations recorded from the Mesoarchean to the Paleoproterzoic have been linked to the evolution of the biogeochemical cycle of nitrogen toward its modern –microbially mediated- web of reactions. The biogeochemistry of nitrogen is strongly dependent upon oxidation-reduction reactions, and thus secular variations in $\delta^{15}N$ most probably underline the protracted oxygenation of Earth's oceans and atmosphere, during a period of roughly 700 Ma between 2.7 and 2.0 Ga.

This contribution provides a synthesis of observations made so far from Archean to Mesoproterozoic sedimentary environments. We present an extensive $\delta^{15}N$ database: 874 published $\delta^{15}N$ values measured on various sedimentary lithologies and phases, including kerogen, phyllosilicates, shales, carbonates, cherts, Banded Iron Formations and N_2-bearing fluid inclusions. The compilation spans from 3.8 Ga to 1.4 Ga and we use statistical methods (Gaussian Kernel functions) applied to geochemical times series for its analysis.

Accordingly, we suggest that the anaerobic process of nitrogen fixation and ammonium assimilation evolved early in biological evolution during the Paleoarchean or earlier. Meso- to Neoarchean ^{15}N enrichment of +15‰ in average and up to +50‰ most probably record the initiation of the oxidative part of the nitrogen cycle including nitrification and denitrification. A second positive nitrogen isotope excursion is recorded during the Paleoproterozoic at around 2.0 Ga and might reflect the fluctuation of a redox transition zone where NH_4^+ would be present in the deep anoxic ocean and NO_2^- and NO_3^- would accumulate above the oxic-anoxic interface in response to increasing atmospheric and oceanic oxygen concentrations. A complete nitrogen biogeochemical cycle including its oxidative part might thus be recorded since the Paleoproterozïc, in line with the view that free oxygen had stabilized NO_3^- in the surface oceans by that time. Increasing number of $\delta^{15}N$ measurements through the Precambrain rocks record would help to refine these interpretations.

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