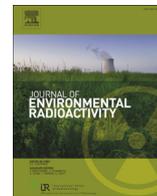




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Modelling of the dissolution and reprecipitation of uranium under oxidising conditions in the zone of shallow groundwater circulation



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ABSTRACT

Generic hydrochemical modelling of a granitoid-groundwater system, using the Russian software “HydroGeo”, has been carried out with an emphasis on simulating the accumulation of uranium in the aqueous phase. The baseline model run simulates shallow granitoid aquifers (U content 5 ppm) under conditions broadly representative of southern Norway and southwestern Siberia: i.e. temperature 10 °C, equilibrated with a soil gas partial CO₂ pressure (P_{CO2}, open system) of 10^{-2.5} atm. and a mildly oxidising redox environment (Eh = +50 mV). Modelling indicates that aqueous uranium accumulates in parallel with total dissolved solids (or groundwater mineralisation *M* – regarded as an indicator of degree of hydrochemical evolution), accumulating most rapidly when *M* = 550–1000 mg L⁻¹. Accumulation slows at the onset of saturation and precipitation of secondary uranium minerals at *M* = c. 1000 mg L⁻¹ (which, under baseline modelling conditions, also corresponds approximately to calcite saturation and transition to Na-HCO₃ hydrofacies). The secondary minerals are typically “black” uranium oxides of mixed oxidation state (e.g. U₃O₇ and U₄O₉). For rock U content of 5–50 ppm, it is possible to generate a wide variety of aqueous uranium concentrations, up to a maximum of just over 1 mg L⁻¹, but with typical concentrations of up to 10 μg L⁻¹ for modest degrees of hydrochemical maturity (as indicated by *M*). These observations correspond extremely well with real groundwater analyses from the Altai-Sayan region of Russia and Norwegian crystalline bedrock aquifers. The timing (with respect to *M*) and degree of aqueous uranium accumulation are also sensitive to Eh (greater mobilisation at higher Eh), uranium content of rocks (aqueous concentration increases as rock content increases) and P_{CO2} (low P_{CO2} favours higher pH, rapid accumulation of aqueous U and earlier saturation with respect to uranium minerals).

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1. Introduction

The occurrence of natural uranium in surface- and groundwaters has obvious importance for human health and drinking water policy (Reimann and Banks, 2004; WHO, 2012; Frengstad and Banks, 2014); moreover, it has implications for ore formation and

prospecting. The mechanisms of uranium accumulation in the aqueous phase and its behaviour in natural waters are topics that have occupied many scientists (Lisitsin, 1971; Grenthe et al., 1992; Kislyakov and Shchetochkin, 2000; Barnett et al., 2000; Runde, 2000; Bain et al., 2001; Kondratyeva and Nesterova, 2002; Barsukov and Borisov, 2003; Krainov et al., 2004; Shvartsev et al., 2007; Dutova and Nikitenkov, 2010; Frengstad and Banks, 2008, 2014; Ariunbileg et al., 2016). It is broadly recognised that, while uranium forms a variety of uranium (+VI) oxy-ions and complex ions that permit its accumulation and mobilisation in relatively high concentrations in oxidising aqueous environments, its behaviour is redox-sensitive. The mobility of uranium in reducing environments can be severely limited, at least at circum-neutral pH,

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by the formation of reduced (uranium (+IV)) secondary minerals. This is also the reason why primary uranium deposits tend to be formed in redox-front (e.g. “roll-front”) environment (such uranium deposits formed by precipitation from aqueous solution are typically termed “hydrogene” in Russian terminology). Although laboratory and field studies have allowed a generally good understanding of the occurrence and behaviour of aqueous uranium, some uncertainties remain. Does uranium (+VI) reach concentrations which represent an “equilibrium” with a given mineral assemblage? To what extent can it continue to accumulate in the aqueous phase before reaching a mineral saturation “ceiling”? Do observed high concentrations (e.g. in the mg L⁻¹ range: Frengstad et al., 2000; Frengstad and Banks, 2014) represent some form of supersaturated state, with mineral precipitation limited only by kinetic constraints?

This paper represents a continuation of the research carried out by the Tomsk research team (Bukaty et al., 2010; Dutova and Nikitenkov, 2010) and focuses on the behaviour of uranium in oxidising conditions in the zone of shallow groundwater circulation (often referred to in Russian literature as the “hypergene” zone). Such conditions are, of course, widely encountered by hydrogeologists and geochemists, not least in the context of uranium toxicity in potable groundwater (Frengstad and Banks, 2014). In a Russian context, we consider especially groundwater discharge areas adjacent to the folded, metamorphic and igneous cores of orogenic belts - regarded as being favourable for the accumulation of hydrogene uranium deposits (Kondratyeva et al., 1980). The methods used for the physico-chemical modelling of uranium in this paper have been selected to best reflect the natural conditions, pH and redox ranges encountered in Russian field studies (Lisitsin, 1996; Barsukov and Borisov, 2003; Bukaty, 2005a; Shvartsev et al., 2007; Bukaty et al., 2010; Chudnenko, 2010).

2. Software and methods

2.1. The HydroGeo code

The software package “HydroGeo”, developed by M.B. Bukaty, has been selected as the preferred modelling tool for the study of uranium hydrochemistry reported here (Bukaty, 2002, 2005a, 2005b, 2008). HydroGeo, like many other similar models developed in western Europe or the USA (such as MINTEQA or PHREEQC; Allison et al., 1991; Parkhurst and Appelo, 1999), models the thermodynamic processes of dissolution and precipitation, solving for minimisation of free energy. Like other models, it relies upon a comprehensive database of thermodynamic data for minerals and reactions. Unlike the standard versions of some other modelling tools, however, it does have access to databases which include data on the thermodynamic properties of uranium minerals and species, culled from various sources including cprons92, SUPCRT (Helgeson et al., 1978; Johnson et al., 1992; Arthur, 2001; Anderson, 2009), UNITERM (Shvarov and Bastrakov, 1999; Cleverley and Bastrakov, 2005), Berman (1988), and the NAGRA NTB report series.

For readers unfamiliar with this type of hydrogeochemical modelling, such models essentially start with a set of initial components (mineral assemblage, water and CO₂). These components are allowed to react with each other by solving a large set of simultaneous equations, each equation representing the thermodynamic equilibrium between two (or occasionally more) species. Constraints can be imposed on certain reactions (kinetic constraints, or specification of which minerals are allowed to precipitate when they become supersaturated), but the model ultimately seeks the solution to the large set of simultaneous equations within these constraints. The model keeps internal account of all dissolved species (such as protons, dissolved CO₂, redox-sensitive species or

uranium species, such as UO₂OH⁺), such that pH, Eh, total dissolved solutes (mineralisation) or total dissolved uranium can be calculated at any stage of the simulated hydrochemical evolution. The detail of such modelling is beyond the scope of this paper, but the interested reader is referred to Kharaka et al. (1988), Allison et al. (1991), Parkhurst and Appelo (1999), Ball and Nordstrom (2001), Alekseev et al. (2005) and Bukaty (2002, 2005a, 2005b).

The HydroGeo model has been extensively tested against comparable international models, including the HVM model (Harvie et al., 1984; Bukaty, 2005b). The use of the software HydroGeo for solving various problems has demonstrated earlier by Shvartsev and Dutova (2001), Dutova et al. (2006), Gaskova et al. (2009), Dutova and Nikitenkov (2010), Dutova et al. (2016) and Balobanenko et al. (2016).

2.2. Defining the modelled problem

In this study, the model considered the interaction of groundwater with granitoids under conditions characteristic of the zone of shallow groundwater circulation (temperature = 10°C, pressure = 1 MPa, equivalent to 100 m hydraulic head or 10 bars). The uranium content of the rocks, assumed to be present within the primary mineral phases, was set at between 5 ppm and 500 ppm. The environment was simulated as mildly oxidising, with an initial Eh of between +5 and +100 mV (although the Eh was allowed to vary as the reaction progresses). The model assumes a system which is open with respect to CO₂, equilibrated with various putative soil gas partial pressures (P_{CO2} = 10^{-0.5}, 10^{-1.5}, 10^{-2.5} atm.). Henceforth in this paper, the term “partial pressure” will refer to the (soil) gas-phase partial pressure with which the water is equilibrated. This situation is believed to be characteristic of groundwater drainage from granitoid-containing hydrogeological massifs. Naturally, the higher the P_{CO2}, the lower the initial water pH.

The composition of the simulated granitoid mineral assemblage was broadly based on the composition of granitoids that are common in mountainous areas of southwestern Siberia (Western and Eastern Sayan mountains, Kuznetsk Alatau, Altai, Salair and the Kolyvan'-Tomsk folded zone - Babin et al., 2007; Banks et al., 2008, 2011; Korobeinikov et al., 1983; Voroshilov et al., 2014). These are predominantly Cambro-Ordovician granitoids intruded into a Precambrian-Cambrian suite of metavolcanics and metasediments. Specifically, the modelling assumed an assemblage comprising 60% plagioclase (An₃₀Ab₇₀), 23% quartz, 5% hornblende, 7% biotite and 5% potassium feldspar. Calcite is initially assumed to be absent. The parent mineral assemblage is indicated in Table 1. The uranium was introduced in the model in its hexavalent form as a substitute for Ca and Al proportionately in the matrices of all of the aluminosilicate mineral phases (except quartz) listed in Table 1. Accordingly, uranium is released to the water phase as the minerals are hydrolysed.

The rate of dissolution/hydrolysis of the various mineral phases is calculated on the basis of initial reaction/dissolution rate constants, relative to a reference reaction. As reaction products accumulate in the aqueous phase and equilibrium is approached, the net rates of reaction decrease according to the relevant rate laws. Precipitation, once saturation has been achieved with respect to the secondary minerals, is assumed to be instantaneous. Sorption is not explicitly included in these simulations.

The modelling of the aqueous phase considered redox potential and the following main ionic components (and their aqueous complex ions): H⁺/OH⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe²⁺/Fe³⁺, Al³⁺, SO₄²⁻, Cl⁻. The following uranium species were also considered within the model: (UO₂)²⁺, U⁴⁺, (UO₂HCO₃)⁺, UO₂(HCO₃)₂, UO₂CO₃, (UO₂(CO₃)₂)²⁻, (UO₂(CO₃)₃)⁴⁻, (UO₂(CO₃)₃)⁵⁻, ((UO₂)₂CO₃(OH)₃)⁻, (U(CO₃)₄)⁴⁻, (U(CO₃)₅)⁶⁻, UO₂SO₄, (UO₂(SO₄)₂)²⁻, UO₂(HSO₄)₂,

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