

## Thermodynamic modelling

Thermodynamic modelling was done using the software package Geochemist's Workbench 12® (GWB; Bethke, 2007). For stability diagrams, the phase 2 and P2plot GWB application and for solubility calculations during fluid cooling, the react GWB application was used. Calculations were done with a linear stepsize for  $\log(fO_2)$ - $pH$  diagrams and a logarithmic stepsize for mineral dissolution and fluid cooling of less than 0.001 (delxi x and y). The total mass of the system was fixed to 1 kg of H<sub>2</sub>O.

For ore stage II calculations, the fluid charge imbalance was neutralized with Cl<sup>-</sup> since the relative change in Cl with respect to the high salinity is insignificant. The internally consistent Thermoddem June 2017 database version with the addition of rammelsbergite and gersdorffite from Scharrer et al. (2019) was used. Furthermore,  $\Delta_f G$  of the pure As endmember of the jordanite-gratonite solid solution (between 0 and 300 °C) was roughly estimated by the method of Craig and Barton (1973), who empirically showed that the  $\Delta_{reaction} G$  from simple sulfides is usually less negative than the hypothetical ideal energy of mixing. To keep internal consistency, the simple sulfides orpiment (As<sub>2</sub>S<sub>3</sub>) and galena (PbS) from the Thermoddem database were used as a basis for  $\Delta_f G$  estimations.

For modelling the supergene remobilization processes, the thermos.comV8.R6+ GWB thermodynamic database was used due to the abundantly present arsenates, aqueous arsenic species, and aqueous uranium species. All calculations considering supergene processes were done at 25 °C. For the uranyl arsenate calculations, no charge balancing was done on Cl due to the minimal initial Cl content of the fluid and because the Cl content strongly defines the stability of mimetite. However, Cu-, Pb- and Ba uranyl arsenates of the composition M<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> xL (where M are divalent metal cation and UO<sub>2</sub><sup>2+</sup> and L is H<sub>2</sub>O) are missing in the thermodynamic database and reliable thermodynamic data is sparse. Thus these have been

implemented from experimental studies (zeunerite) or estimated (hallimontite). For stability calculations, all aqueous species and the following minerals were considered: anglesite, arsenolite, brochantite, chalcocite, chalcopyrite, cuprite, galena, hallimondite, hematite, litharge, mimetite, nat. As, sphalerite, realgar, tenorite, uraninite, zeunerite).

Three publications, Van Genderen and Van Der Weijden (1984), Vochten and Goeminne (1984) and Zhil'tsova et al. (1987), present solubility data for the Cu-uranyl arsenate zeunerite/meta-zeunerite ( $\log K$  is -42.2, -49.2 and 49.96, respectively). We discarded the solubility data from Van Genderen and Van Der Weijden (1984), as it is estimated and only considers the anhydrous version of the mineral whereas the latter two are based on experimental work and consider the naturally occurring hydrated versions. The presented solubility data from Vochten and Goeminne (1984) correspond to a  $\Delta_f G$  of -5315 kJ/mol for meta-zeunerite,  $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ .

Due to the lack of thermodynamic data for Pb-bearing uranylarsenates, we roughly estimated  $\Delta_f G$  for hallimondite. Arsenates and phosphates are commonly structurally related so that substantial substitution between As and P is possible (e.g., Liu et al., 2014). The  $\Delta_f G$  of arsenates is always more positive than that of the respective phosphate counterpart (see e.g., in the thermodynamic database [thermos.com](https://thermos.com) V8.R6+). Considering minerals of the  $\text{M}_3\text{X}_2 \cdot x\text{L}$  composition (where M are divalent metal cation or  $\text{UO}_2^{2+}$ , X is  $\text{AsO}_4^{3-}$  or  $\text{PO}_4^{3-}$  and L is  $\text{H}_2\text{O}$ ), the absolute difference in  $\Delta_f G$  between arsenates and phosphates ranges from -680 kJ/mol to -820 kJ/mol with an average around -760 kJ/mol (13 mineral pairs with data from the [thermos.com](https://thermos.com) V8.R6+ database and the following compilations: Tardy and Vieillard, 1977; Wagman et al., 1982; Barin, 1995; Davis et al., 1996; Ryu et al., 2002; Nriagu and Moore, 2012). The minerals  $(\text{UO}_2)_3\text{X}_2$  present a difference of -805,  $\text{Pb}_3\text{X}_2$  of -785 kJ/mol or -810 kJ/mol, depending if the  $\text{Pb}_3(\text{AsO}_4)_2$  data of Davis et al. (1996) or Barin (1995) are considered. Thus, we assume that the  $\Delta_f G$  of the arsenate hallimondite, which is a compositional 2:1 mixture

of the Pb and UO<sub>2</sub> groups, is 800±15 kJ/mol more positive than its phosphate counterpart (parsonsite) for which data exist. Calculating the stability of hallimondite from parsonsite is reasonable since both minerals are isostructural (Walenta, 1965; Locock et al., 2005; Plášil et al., 2009). The resulting  $\Delta_f G$  is -3012±15 kJ/mol, which is slightly more negative than the ideal mixing scenario of the two endmembers (Pb- and UO<sub>2</sub>-arsenate), assuming a  $\Delta_f G$  contribution of 236,1 kJ/mol per H<sub>2</sub>O molecule (value suggested by Glasser, 2013).

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