

Modelling the vapour transport of Au, Ag, and Cu chlorides at high temperature based on new experimental data

ART. A. MIGDISOV^{1*}, N. HURTIG¹, AND A.E. WILLIAMS-JONES¹

¹McGill University, Earth & Planet. Sci., Montreal, QC, Canada (*correspondence: artas65@gmail.com)

The fact that water can significantly increase the gaseous transport of weakly volatile compounds has been long-known and is attributed to hydration, namely the formation of gaseous clusters involving H₂O molecules. However, laboratory experiments performed in simple H₂O-bearing systems have yielded concentrations of metals, e.g., Cu and Au, considerably lower than reported for vapour inclusions in many natural samples. Furthermore, calculations of the stability of known Cu- and Au-bearing gaseous clusters have shown that these clusters cannot explain the very high concentrations Cu and Au predicted for some vapour-dominated hydrothermal systems. Assuming that the source of this disagreement lies in the models that have been developed for the hydration process, we have re-visited the Au-HCl-H₂O, AgCl-HCl-H₂O, CuCl-HCl-H₂O, and CuCl₂-HCl-H₂O systems, and conducted additional experiments that allow us to more accurately determine the hydration numbers of metal-bearing gas clusters.

Our experiments involved determining the solubility of metal chlorides (or metals) in HCl-bearing water vapour at a variety of water vapour pressures and temperatures ranging from 300 to 450 °C. The experimental technique employed in this study is identical to that reported in our previous publications [1]. The data obtained from these experiments demonstrate that, in contrast to conclusions in our earlier publications, hydration numbers of metal-bearing clusters are not constant, but increase with increasing fugacity of water. This results in an exponential increase in the saturation concentrations of metals in water vapour at elevated pressures and temperatures.

We fitted our experimental data to a simplified model similar to that developed by Pitzer and Pabalan [2] for the solubility of NaCl in low-density fluids. The model accounts for a set of hydrated species of the common stoichiometry MeCl(H₂O)_n, where n ranges from 1 to 14. After independent treatment of each of the experimental isotherms, it was found that the Gibbs free energy of each of the modelled clusters varies linearly with the reciprocal absolute temperature (1/TK). This allows extrapolation of the data collected at 300 to 450 °C to much higher temperatures. The new model has been tested against the measurements of Simon et al. [3] for the solubility of Au and Ag at 1000 to 1400 bar and 800° and yield reasonable results. In addition, the concentrations of Ag and Au (the experiments on Cu are still in progress) calculated for 500 °C show much closer approximation to those determined in natural fluid inclusions than in any previous models

[1] Archibald et al. (2001) *Geochim. Cosmochim. Acta*, 65, 4413

[2] Pitzer and Pabalan (1986) *Geochim. Cosmochim. Acta*, 50, 1445

[3] Simon et al. (2005) *Geochim. Cosmochim. Acta*, 69, 3321

The role of changing abstraction patterns in the contamination of a low-arsenic aquifer in Bangladesh

I. MIHAJLOV^{1*}, M. STUTE^{1,2}, B.C. BOSTICK¹, I. CHOUDHURY³, K.M. AHMED³ AND A. VAN GEEN¹

¹Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY, USA, mihajlov@ldeo.columbia.edu (* presenting author)

²Barnard College, New York, USA

³Dhaka University, Dhaka, Bangladesh

The installation of deeper aquifer community wells has been one of the primary arsenic mitigation strategies in Bangladesh, a country where a large portion of shallow tubewell groundwaters exceed the WHO limit of 10 µg/L As. Shifting groundwater abstraction patterns, in particular the increased pumping from deeper aquifers, could potentially threaten this resource by vertical transport of As and organics between aquifers and across leaky confining units. While this scenario has been addressed by Bengal basin-wide models [1], hydrogeologic conditions across the basin are variable.

Our study focused on a site 25 km east of Dhaka where a community well was installed twice in a low-As aquifer separated from the shallow aquifer by >10m of silty clay, but As levels in both wells rose within <18 months. An increasing downward hydraulic gradient across clay units in the vicinity, as well as a lack of evidence of mechanical failures at the site, led us to suspect vertical leakage across the clay. Thus, a network of pumping and monitoring wells was established on the site to conduct pumping tests and continuously monitor hydraulic heads. Lithologs, sediment X-ray fluorescence (XRF) and chemical extraction profiles were collected during well installation, and groundwater was sampled for water chemistry, DIC ¹³C and ¹⁴C, ²H, ¹⁸O, ³H, and noble gas analysis.

Lithologs and XRF profiles established that stratigraphy and sediment composition were laterally uniform. Pumping from long-screen wells in either aquifer did not induce measurable drawdown in the other, but the time plot of drawdown in the confined aquifer was characteristic of a leaky aquifer. Given the present downward hydraulic gradient of ~1m between the aquifers, continuous slow downward transport of As and/or organics across the clay may exist.

High-As groundwater is absent at the depth of the community well failures, but the upper ~10m of the aquifer (below the clay) is ³H-dead and displayed high dissolved conc. of Fe, As, and NH₃. The well-advanced reduction in this stratum was accompanied by elevated Na, DOC, and DIC levels, and a lower pH. Depressed ¹⁴C and heavy ¹³C signature of the DIC there, along with low diss. [Ca], was characteristic of microbial consumption of old organic C (potentially leached from the clay with Na) and methanogenesis. Water level and ³H data, however, also implied that a flow of recently recharged water exists below this upper portion of the aquifer, presumably due to pumping from a nearby factory. While the community wells probably failed due to vertical transport of As within the aquifer itself, it is presently unclear if the source of As and DOC in the upper part of the aquifer is from clay leakage or if that layer is a zone of low flow where resident organic C is currently consumed.

[1] Radloff et al. (2011) *Nature Geoscience* 4, 793-798.