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The transport of bismuth in HCl-bearing aqueous vapour and vapour-like supercritical fluids

DR. XINSONG WANG[1], A.E. WILLIAMS-JONES[2], QI LIU[1], FEI-XIANG LIU[1], RUI-ZHONG HU[1], DR. YUAN MEI[3], ZI-QI JIANG[1], LIN-BO SHANG[1], JING-JING ZHU[1] AND XIAN-WU BI[1]

[1]Institute of Geochemistry, Chinese Academy of Sciences
[2]McGill University
[3]CSIRO Mineral Resources

Presenting Author: wangxinsong@mail.gyig.ac.cn

Hydration by H_2O clusters has been shown to be an important means of transporting metals in hydrothermal vapours and vapour-like supercritical hydrothermal fluids, however, how hydration affects the transport of relatively volatile elements like bismuth has not been evaluated. This is important to know because bismuth is a key pathfinder for gold in many intrusion-related gold ore-forming systems, where aqueous vapour- and vapour-like supercritical fluids can play an essential role in metal transport. In order to shed light on the behaviour of bismuth in such fluids, we carried out experiments to investigate the solubility and speciation of bismuth in HCl-bearing aqueous vapour and low to intermediate density supercritical HCl-bearing aqueous fluids at temperatures up to 400 °C. The results show that two bismuth species were present in the HCl-bearing fluids ($X_{HCl} > 0.0005$), namely $BiCl_{3,g}$ at low fH_2O and $BiCl_3(H_2O)_{n,g}$ at higher fH_2O. Our data clearly show that $BiCl_{3,g}$ is highly volatile at low water fugacity, acting as an anhydrous gas in relatively dry fluids. At higher water fugacity, the $BiCl_{3,g}$ molecule reacts with clusters of water molecules to form hydrated species. Significantly, the stability of hydrated bismuth species, $BiCl_3(H_2O)_{n,g}$, with low hydration numbers is lower than that of the anhydrous species, $BiCl_{3,g}$, resulting in a decrease in bismuth solubility with increasing fH_2O. However, at a threshold of water fugacity that increases with increasing temperature, the hydration number and the solubility of hydrated species ($BiCl_3(H_2O)_{n,g}$) increase with increasing water fugacity and the density of the fluid. Consequently, anhydrous bismuth gaseous species increase in importance with increasing temperature and become dominant at temperatures >500 °C in fluids that have moderate density. Hydrated bismuth species are dominant in vapours and vapour-like aqueous fluids at lower temperature that have high density. Thus, the aqueous vapour-like supercritical fluids that exsolve from magmas to form intrusion-related gold deposits can transport large amounts of bismuth, potentially explaining why bismuth is able to act as an important pathfinder for these types of gold deposits.