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In-situ Raman Spectroscopic Investigation on the Speciation of Copper in Hydrothermal Fluids at Temperatures up to 300 ^{o}C

LIN-BO SHANG[1], ZHENG-LONG WANG[1,2], I-MING CHOU[3] AND XIAN-WU BI[1]

[1]Institute of Geochemistry, Chinese Academy of Sciences
[2]University of Chinese Academy of Sciences
[3]Institute of Deep-sea Science and Engineering, Chinese Academy of Sciences

Copper predominantly occurs in the Cu^{+} and Cu^{2+} oxidation states, which can interconvert under varying redox conditions. In chloride-rich geological fluids, Cu-Cl complexes are widely recognized as the primary agents responsible for copper solubility, transport, and enrichment[1]. Investigating copper speciation and the interconversion between its oxidation states is crucial for understanding the mechanisms of copper migration in diverse hydrothermal environments. spectrophotometric experiments can provide direct information on the nature of the complexes[2-5], In this study, we employed the recently developed in situ Raman spectroscopy with P_{H2} control method[6] to examine copper speciation in hydrothermal systems under saturated vapor pressures at temperatures ranging from 24 to 300 ℃. As shown in figure 1, our findings reveal that in the Cu+HCl system, copper dissolves in the hydrothermal solution primarily as a monovalent copper chloride complex. At elevated temperatures (>200 ℃), $CuCl_2^-$ emerges as the predominant species, whereas at lower temperatures and high hydrochloric acid concentrations, $CuCl_3^{2-}$ becomes the dominant species. In the divalent copper chloride hydrothermal system, it is speculated that the dominant copper species transitions from $Cu(H_2O)_n^{2+}$ at low temperatures (<50 ℃) to $CuCl_4^{2-}$ at 100 ℃, and further to $CuCl^+$ and $CuCl_2^0$ at 300 ℃. Upon the introduction of a reducing agent ($K_2S_2O_3/H_2$), the transformation from Cu^{2+} to Cu^+ was observed, with Cu^+-Cl complexes becoming predominant, accompanied by partial copper precipitation. This suggests that a decrease of oxygen fugacity represents an important mechanism governing the deposition and enrichment of copper.

References

[1] Xiao Z.F. et al., (1998). *Geochimica et Cosmochimica Acta*, 62, 2949–2964.

[2] Collings, M.D. et al. (2000). *Chemical Geology,* 167, 65–73.

[3] Fulton, J.L. et al. (2000). *Chemical Physics Letters,* 330, 300–308

[4] Brugger J. et al. (2001) *Geochimica et Cosmochimica Acta*, 65, 2691–2708.

[5] Applegarth, L.M.S.G.A. et al. (2014). *The Journal of Physical Chemistry B,* 118, 204–214

[6] Chou, I.M. et al. (2021). *Geochemical Perspectives Letters*, 20, 1–5.

Figure 1. In situ Raman spectra monitoring the variation of Cu-Cl species as a function of temperature ranging from 24 to 300 °C : (a) Cu + 2 m HCl system; (b) 1 m $CuCl_2$ system.