Copper complexes in thiosulfate-ammonia-chloride brines

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Thiosulfate is a metastable ligand which is not always considered in geochemical transport models; however, studies[2,3] suggest it may be important for transporting metals in geological environments and for producing anomalous geochemical signatures. For example, thiosulfate can be generated in situ by the oxidation of pyrite in ground waters by several pathways[1], a process that may take place upon mixing hydrothermal fluids with meteoric waters[3].

In this study we investigate Cu complex formation in the $Cu(II)/Cu(I)$-NH_3-S_2O_3-Cl system using UV-Vis spectroscopy to measure changes in Cu speciation. The binary $(Cu(I)$-$Cl)$ and ternary subsystems $(Cu(I)$-NH_3-Cl, $Cu(I)$-S_2O_3-$Cl)$ were studied initially. Figure 1 shows the UV spectra of $Cu(I)$-S_2O_3-Cl solutions, where at low $[S_2O_3]/[Cu(I)]$ (<0.5) the dominant species is a $Cu(I)$-Cl complex (275 nm), while at higher $[S_2O_3]/[Cu(I)]$ ratios of 2-10 the dominant species are $Cu(I)$-S_2O_3 complexes (230-250nm). Quantitative analysis of the spectra suggests that one or more mixed complexes of $Cu(I)$-Cl-S_2O_3 were present, e.g. $[CuCl(S_2O_3)]^{2-}$ (log _ = 9.044) and $[CuCl_2(S_2O_3)]^{3-}$ (log _ = 7.860).
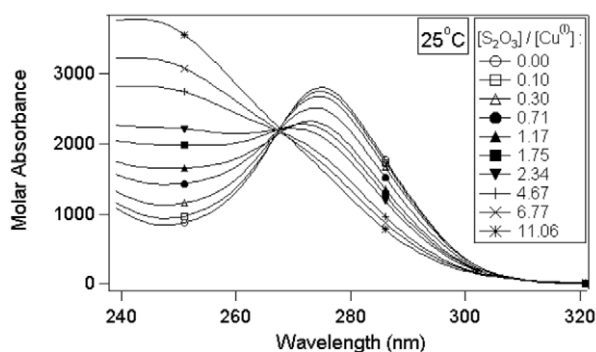
Figure 1: Ultraviolet spectra for the $Cu(I)$-S_2O_3-Cl system. $[Cl^-]$ = 2M; $[Cu^+]$ = 2×10^{-4}M.

Our derived formation constants can be used in predictive models of copper transport in groundwater systems, and to understand better the controls on mineral dissolution and/or precipitation reactions, redox processes and metal adsorption.

References

1. Aylmore, M.G. and Muir, D.M. (2001) *Min. Eng.*, **14**, 135-174.
2. Bowell, R.J., Foster, R.P. and Gize, A.P. (1993) *Eco. Geo.*, **88**, 999-1016.
3. Webster, J.G. (1987) *App. Geochem.*, **2**, 579-584.

The origin of rhyolite magmas and their 'phenocrysts'

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A paradox exists where the whole rock compositions in a magma series are explained by continuous removal of crystals (fractional crystallization) but the rocks contain abundant phenocrysts. This paradox is resolved here by comparing observed correlations between whole rock and glass compositions, crystallinity, crystal zoning, and eruption temperature (from Fe-Ti oxides) with predictions from phase diagrams. Hornblende-bearing rhyolites from the 530 km^3 Oruanui eruption and several pre-Oruanui volcanics (Taupo, New Zealand) have compositions consistent with fractional crystallization yet contain 5 to 30% crystals. Temperature correlates weakly with whole rock composition but strongly with glass composition, defining a liquidus similar to that expected at 200 to 300 MPa under water saturation. Glass and whole rock compositions lie on the same compositional trends, and the liquidus temperatures of the whole rocks, predicted from the liquidus of the glass compositions, are matched by whole rock zircon-saturation temperatures. This indicates that the whole rocks have liquid compositions. Modal % phenocrysts increase with the difference between the calculated whole rock liquidus and magma temperatures at a rate of 4.3% crystallization per 10 °C cooling, a value similar to those reported by experimental petrologists. Plagioclase, the major phenocryst phase, shows normal zonation in K_2O which, in most cases, is consistent with fractional crystallization of the whole rock composition by an amount represented by the phenocryst content.

Most of the crystals in the Oruanui and consanguineous rhyolites predominantly grew during cooling of the magma after fractional crystallization had generated the whole rock composition. Remaining crystals (notably some zircons) represent material from an earlier stage of rhyolite generation. At least three stages of silicic magma evolution are thus required. First, fractional crystallization of a parental rhyolite (or dacite) produced a range of more-evolved rhyolitic liquids. Second, these liquids separated efficiently from their crystal residues. Third, the separated liquids cooled by several tens of degrees and grew phenocrysts that remained suspended in the viscous magma. This requires that the rhyolites were not erupted directly from their point of generation..