

## Speciation and thermodynamic properties of Manganese(II) and Nickel(II) chloride complexes in hydrothermal fluids: *In situ* XAS study

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Aqueous Mn (II) and Ni (II) chloride complexes play an important role in Mn/Ni transport and deposition in hydrothermal ore-forming systems. Understanding metal transport and deposition relies on our knowledge of the metal speciation transported in hydrothermal fluids and thermodynamic properties of each species.

Synchrotron based XAS technique was used to measure *k*-edge spectra of Mn (II) and Ni (II)-bearing solutions with increasing temperature and salinity. Mn (II) and Ni (II) exhibit similar XANES spectral evolutions to other divalent transition metals, which reveals that octahedral species predominante at room temperature, while tetrahedral species become more important with increasing temperature and salinity. *Ab initio* XANES simulations and EXAFS refinements determined the structure of predominant end-member species  $M(H_2O)_6^{2+}$  and  $MCl_3(H_2O)$  and demonstrated that fully chlorinated complex  $MCl_4^{2-}$  is not stable in hypersaline brines ( $M = Mn, Ni$ ). This result, together with previous studies of aqueous chloride complexes of Fe (II)[1] and Co (II)[2] revealed the difference in the two pairs of transition metals to form high order chloride complexes: Mn-Fe and Ni-Co. The former member forms  $MCl_3(H_2O)$  at high temperature and high salinity while latter member forms fully chlorinated complex under the same conditions. XANES spectra were used to calculate formation constants and thermodynamic properties of  $MCl_3(H_2O)$  species which can explain the strong fractionation between the proposed couple metals in hydrothermal systems.

[1] Testemale *et al.* (2009) *Chemical Geology* **264**, 295–310.

[2] Liu *et al.* (2011) *Geochim. Cosmochim. Acta* **75**, 1227–1248.

## Craton destabilization and alkaline magmatism in equatorial East Africa

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Several types of alkaline magmatism are typically related to specific locations on and around cratons. Diamond-bearing kimberlites are restricted to craton centres, many lamproites occur around craton edges, and ultramafic lamprophyres are associated with areas where cratons are rifted. The Tanzanian craton is an example of a craton at an intermediate stage of destabilization. It is supported by warm upwelling mantle and its surface is at an elevation of >1, 100m. However, unravelling the petrogenesis is complicated by the confluence of cratonic magmatism with the East African Rift. We have reassessed alkaline magmatism around the Tanzanian craton and find a negative correlation between K/Na ratios in rocks and distance from the craton. Potassium-rich rocks have generally been associated with the western rift branch because of the occurrence of kalsilite-bearing volcanic rocks there, but also occur at the eastern edge of the craton. The association of potassium with cratons is attributed to melting at >140 km depth to form mixed source regions containing phlogopite pyroxenite and peridotite. In the western branch of the rift, the base of the lithosphere is interpreted to plunge to deeper levels towards the north beneath a saddle of cratonic lithosphere that links the Tanzanian and Congo cratons [1]. K/Na of magmas decreases towards the south where melting occurs closer to the surface. Here, amphibole rather than phlogopite is involved in melting. In southern Kenya (eastern rift), olivine phenocrysts have high Ni contents that are interpreted to indicate melting of a different type pyroxenite, namely garnet pyroxenites that are also found as xenoliths [2]. Due to the combination of craton destabilization and continental rifting, the pattern of magmatism around the Tanzanian craton shows a great variety of contemporaneous magmatism which is similar to that stretched over more than 1, 200 million years during several stages in the Labrador Sea rift [3].

[1] Link *et al.* (2010) *Int. J. Earth Sci.* **99**, 1599–1611.

[2] Kaeser *et al.* (2009) *Contrib. Mineral. Petrol.* **157**, 453–472. [3] Tappe *et al.* (2007) *Earth Planet. Sci. Lett.* **256**, 433–454.