

Thermodynamic data for cementitious systems: Katoite

B. LOTHENBACH^{1*}

¹Empa, Concrete & Constr. Chem., Dübendorf, Switzerland

(*correspondence: barbara.lothenbach@empa.ch)

The formation of katoite, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$, is observed experimentally in hydrated calcium aluminate cements but generally not in hydrated Portland cements. Thermodynamical modeling of the stable phases in hydrated Portland cements without calcite predicts either the formation of katoite, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ [1], or monosulfoaluminate, $3\text{CaO}\cdot\text{CaSO}_4\cdot\text{Al}_2\text{O}_3\cdot 12\text{H}_2\text{O}$ [2-4], depending on which thermodynamic data are used.

A recent critical review of the thermodynamic data for katoite resulted in $\Delta_f G^\circ = -5008.2$ kJ/mol and $\Delta_f H^\circ = -5537.3$ kJ/mol [5] using an entropy of 422 J/mol/K and heat capacity of 446 J/mol/K from [6]. It was shown that some of the experimental solubility measurements have been performed on carbonated samples where monocarboaluminate had precipitated [5]. This resulted in too low $\Delta_f G^\circ$ values for katoite in many databases [2-4] and thus to wrong predictions on the stability of katoite as shown in the figure below.

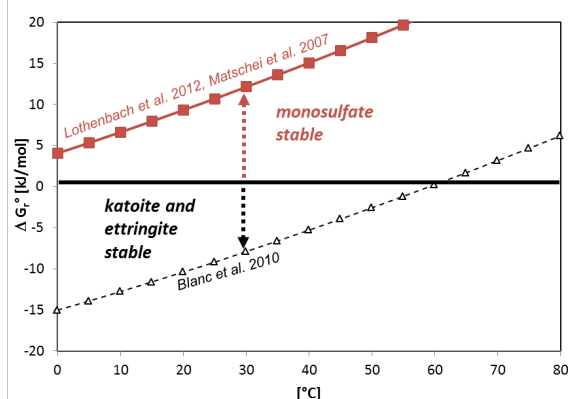


Figure 1: Influence of the stability of katoite on the stability of ettringite and katoite relative to monosulfate in hydrated Portland cements: $3\text{CaO}\cdot 3\text{CaSO}_4\cdot\text{Al}_2\text{O}_3\cdot 32\text{H}_2\text{O} + 2(3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}) \rightleftharpoons 3(3\text{CaO}\cdot\text{CaSO}_4\cdot\text{Al}_2\text{O}_3\cdot 12\text{H}_2\text{O})$.

[1] Matschei *et al.* (2007) *Cem Concr Res* **37**, 1379-1410. [2] P. Blanc *et al.* (2010) *Cem Concr Res* **40**, 1360-1374. [3] Damidot & Glasser (1993) *Cem Concr Res* **23**, 221-238. [4] Lothenbach & Winnefeld (2006) *Cem Concr Res* **36**, 209-226. [5] Lothenbach *et al.* (2012) *Cem Concr Res* **42**, 1621-1634. [6] Geiger *et al.* (2012) *Am Min* **97**, 1252-1255.

Distinctive Composition and Genesis of Copper Ore-forming Arc Magmas

ROBERT R. LOUCKS^{1*}

¹Centre for Exploration Targeting & CCFS, School of Earth and Environment, University of Western Australia, Crawley, WA 6009, Australia

*email: Robert.Loucks@uwa.edu.au

In arc segments undergoing orogenic deformation, magma ascent to shallow depths is inhibited by horizontal compressive stress that hinders dyke propagation and that fosters development of subhorizontal magma chambers deep in the ductile lower crust. Experimental and field evidence shows that distinctive chemical features of Cu-ore-forming arc magmas develop in magma chambers near the Moho where country- rock temperatures on a normal arc geotherm are around 700-800°C, so magma chambers cool slowly and tend to last long enough to experience intermittent influxes of mantle-derived basaltic magmas that mix with residual magma already in the chamber, producing multiple cyclic units in stratified crystal cumulates on the magma chamber floor. Residual dacitic melt fractions eventually acquire extraordinary contents of dissolved H_2O (~10 wt%) and SO_3 and probably Cl by inheritance through many cycles of chamber replenishment and fractional crystallisation. Over many such cycles, residual magmas reach unusually high ferric/ferrous ratios, due to selective segregation of ferrous iron into cumulate silicates. The typically high oxidation states of Cu-ore-forming arc magmas is reflected in part by elevated V/Sc and Eu/Eu* ratios. This high oxidation state endows the magma with exceptional sulfur-carrying capacity, because sulfate is around 100 times more soluble (at anhydrite saturation) than sulfide (at pyrrhotite saturation) in magmas of dacitic to rhyolitic composition. The effects of high pressure and high content of dissolved H_2O are to retard plagioclase crystallisation and promote early and prolific hornblende crystallisation, which causes the ratios (Eu/Eu*)/Yb and Sr/Y to increase in residual melt as differentiation proceeds from basaltic to dacitic compositions.

Values of $\text{Sr/Y} > 35$, $(\text{Eu/Eu}^*)/\text{Yb} > 2$, and $\text{V/Sc} > 10$ at 58-70 wt% SiO_2 are typical of arc magmas parental to magmatic-hydrothermal copper ore deposits throughout Phanerozoic time, according to my compilation of compositions of ore-forming intrusives in >135 deposits. These ratios may be used to screen collections of whole-rock chemical analyses to identify igneous complexes that are prospective (fertile) for copper ore genesis. Hundreds of thousands of such analyses are available in published literature. I have compiled many.