

Geochemical trends across the Palaeoproterozoic Kuruman and Griquatown BIFs, Transvaal Supergroup, South Africa, and implications for the GOE

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The Transvaal Supergroup on the Kaapvaal Craton of South Africa contains one of the thickest (up to ~1000m), most complete, and best preserved sequences of banded iron-formation (BIF) of early Palaeoproterozoic age (~2.5-2.4 Ga). The stratigraphically lower Kuruman BIF exhibits typical microbanded textures dominated by chert and magnetite, with lesser siderite and Fe silicate; it is conformably overlain, through a gradual facies transition, by the granular to microbanded, siderite-Fe silicate-rich Griquatown BIF.

We have carried out a reconnaissance (generally one sample every 10-15m) geochemical study of both the Kuruman and Griquatown BIFs. Our key objective was to test whether these BIFs stratigraphically record geochemical signals of potential relevance to the evolution of the atmosphere-ocean system leading to the Great Oxidation Event (GOE) at ca. 2.4Ga. Our sampling focused on two complementary drillcore intersections located approximately 60 km NW of the town of Kuruman. The two drillcores together capture the entire BIF stratigraphy, which in this specific area measures ~400m thick. The Kuruman BIF is stratigraphically underlain by the Klein Naute black shale that overlies the Campbellrand carbonate sequence at the base of the Transvaal Supergroup, whilst the Griquatown BIF is overlain conformably by the Makganyene diamictite.

Our sample suite captures essentially all major sub-lithofacies of the Transvaal BIFs as described previously [1]. Geochemical results show a number of broad stratigraphic trends: (i) bulk carbonate $\delta^{13}\text{C}$ data range between -6 and -11 per mil, and fluctuate in concert with corresponding fluctuations in the non-ferrous carbonate component of the samples; (ii) Fe and Mn speciation data record a general upward increase in the Mn:Fe ratio of carbonate (and bulk-rock); and, (iii) bulk $\delta^{57}\text{Fe}$ data range between -2.7 and 0.9 per mil, with lower values generally corresponding to samples with high modal siderite relative to magnetite, as seen particularly in the Griquatown BIF.

We regard the stratigraphic increase in the Mn:Fe ratio and attendant decrease in bulk $\delta^{57}\text{Fe}$, as possible precursor signals to the stratigraphically higher, manganiferous and ^{57}Fe -depleted Hotazel Formation, itself thought to have formed prior to the GOE in a highly evolved – chemically and isotopically – stratified marine basin. Mass balance considerations also suggest that C and Fe isotope variations in the BIFs may record primary precipitation from a chemically and isotopically stratified water column, rather than isotopic fractionation related entirely to biogeochemical redox processes during diagenesis.

[1] Beukes and Gutzmer (2008) *Reviews in Economic Geology* **15**, 5-47.

Kinetic theory of crystallization from meta-stable phases

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Abstract

Various kinds of meta-stable phases are formed on the Earth's surface. Most of these phases are amorphous or poorly crystallized nano-particles. These phases can contain various kinds of harmful elements. When we discuss the behavior of these harmful elements contained in the meta-stable phases, we need to estimate the lifetime of the meta-stable phases because these meta-stable phases are transformed to crystalline stable phases. This paper describes a kinetic theory of the crystallization from a metastable phase [1]. The theory assumes that a crystal nucleates only on the surface of a meta-stable phase, the crystal stops growing at a certain size, and the concentration of metal ion in solution is close to the solubility of the meta-stable phase. On the basis of these assumptions, we have derived integral equations for $R(t)$ (crystal ratio as a function of time). We have solved the integral equations with a successive approximation method. When time t is less than t_{inflec} ($=r_{max}/G$, r_{max} : maximum radius of crystal, G : growth rate of crystal), $R(t)$ is close to fourth power of time; when t is larger than t_{inflec} , $R(t)$ is close to an exponential-type function. The kinetic theory has been applied successfully to the transformation of ferrihydrite nanoparticles to goethite or hematite crystals (Fig. 1), and the crystallization of TiO_2 and ZrO_2 . The theory shows that the nucleation rate of crystal essentially determines the crystallization rate, and that induction period is observed when the growth of crystal is slow.

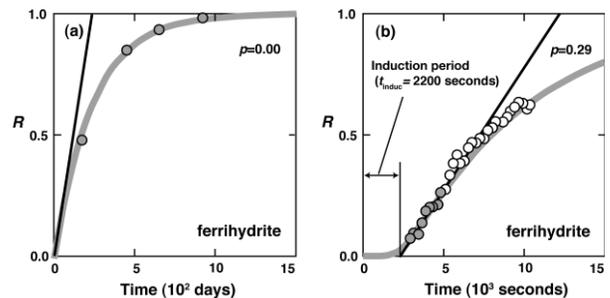


Figure 1: Relation between observed and calculated values of R [1]; (a) the transformation of ferrihydrite at pH 6 and 297 K [2] and (b) the transformation of ferrihydrite at pH 10.7 and 361 K [3]. Circles denote experimental data points and solid curves calculated values based on the present theory. Data points in grey symbols were used for the determination of parameters p and t_{inflec} ($=4/3 t_{induc}$).

[1] Tsukimura et al. (2010) *Crystal Growth & Design* **10**, 3596-3607. [2] Schwertmann et al. (1983) *Clays Clay Mineral.* **90**, 277-1860.

[3] Shaw et al. (2005) *Am. Mineral.* **90**, 1852-1860.