Formation of TiO_2 polymorphs brookite and anatase due to organic-inorganic rock-fluid interactions: Are such processes analogues for the industrial production of TiO_2 nanocrystals?

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Titania polymorphs brookite (subordinately anatase) nanocrystals form during early diagenesis in organic matter-rich mud. Whereas anatase crystals exclusively occur as single crystals, brookite nanocrystals may agglomerate. During further burial, brookite nanocrystals may slightly increase in size. Furthermore, anatase and brookite nanocrystals occur in sedimentary basin situations with organic-inorganic rock-fluid interactions such as at oil-water contacts in oilfields, and along fractures with fluid flow enriched in dissolved organic carbon.

Hydrogeochemical conditions with low pH occur in pore water during early diagenesis in black shales and during oil degradation due to the release of acetic acid, carbon dioxide, etc. This acidic and corrosive environment leads to the release of $Ti^{4+}_{(aq)}$ species from Ti-bearing minerals such as ilmenite and titanite, and the precipitation of brookite and/or anatase. Such conditions and reaction chains are comparable to low temperature sol-gel processes which are applied for the industrial production of nano-sized titania polymorphs.

Theoretical considerations about surface enthalpy and transformation enthalpy are unsuitable to explain the brookite/anatase formation, fate and behaviour in sediments. In sedimentary basins the precipitation of brookite vs. anatase or the transformation from the tetragonal anatase structure into the orthorhombic brookite structure are controlled by a complex mix of interacting factors which, in addition, may change through time and space. According to this, “simple” batch models based on chemical thermodynamic calculations are unsuitable to explain the occurrence of brookite and anatase in black shale. Instead, micro-environments develop in the porewater at low temperature where low pH is coupled to the occurrence of dissolved organic components. Such conditions govern titania nanocrystal precipitation, growth (and potentially agglomeration). Low sedimentation rates retaining a critical geochemical environment or higher temperature seem major controls for the precipitation of anatase and its tendency not to agglomerate.