Thermodynamic analysis of water-rock-hydrocarbon interactions in petroleum systems

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Throughout their evolution across the crust of the Earth, minerals and organic compounds interact in many geological processes ranging from the low-temperature early diagenesis of marine sediments to the metamorphism of pelitic schists. The geochemical cycles of iron, sulfur or nitrogen (among other elements) are governed by such interactions, which correspond to oxidation-reduction reactions. Well-documented examples include the decarbonation of siderite in the presence of carbonaceous matter [1], the formation of sulfur-rich organic matter in carbonate sediments [2], or the exchange of nitrogen isotopes among petroleum and clays in clastic reservoirs [3].

It is the purpose of the present communication to illustrate how thermodynamic properties published for solid and liquid hydrocarbons and sulfur- and nitrogen-bearing compounds of geochemical interest [4,5] can be used to develop quantitative models for the evolution of water-rock-hydrocarbon systems, as well as to make reasonable estimates regarding the composition of petroleum fluids as a function of temperature, pressure, the fugacities of CO_2, H_2S, NH_3 and H_2, and their mineralogical and aqueous environment. Conversely, I will show how compositional data for crude oils can in some instances be used to evaluate or retrieve thermodynamic data.

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The role of arc magmas and subduction-modified lithosphere in ore formation

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Arc magmas are a unique source of subduction-derived volatiles (water, sulfur, and chlorine: mostly derived from seawater-altered oceanic lithosphere), plus water-soluble elements (alkalis and large-ion lithophile elements) and chalcophile and siderophile metals. Upon emplacement in volume in the upper crust, these magmas may generate porphyry Cu±Mo±Au and epithermal Au±Cu deposits. However, during their ascent through the upper plate lithosphere, they interact with these rocks to form hybrid calc-alkaline magmas, and fractionate to leave ultramafic to mafic, amphibolitic cumulate residues at the base of the crust (MASH process of Hildreth and Moorbath, 1988).

Over the life of an arc (typically ≤10–15 m.y.), the mantle wedge above the subduction zone becomes increasingly hydrated and oxidized as slab fluids cause progressive metasomatism, leading to partial melts that also increase in water content and oxidation state over time. Early primitive magmatic fluxes entering the upper plate lithosphere may leave considerable amounts of metals behind in cumulate zones as sulfides separated from relatively reduced (ΔFMQ ≈ 0) magmas (Lee *et al.*, 2012). However, increasing oxidation state in later magmas (ΔFMQ ≈ 1–2) suppresses sulfide-saturation, and leads to efficient transport of metals in magma fluxes reaching the upper crust (Botcharnikov *et al.*, 2011). Consequently, major porphyry-forming events are commonly relatively late in the evolution of a given arc.

The deep crustal residues of arc magmatism are relatively fusible (amphibole-rich) and likely contain small amounts of metal sulfides. Re-melting of these residues during later tectonic events, such as collision or rifting, may generate metalliferous magmas with similar chemical and isotopic characteristics to normal arc magmas, which may go on to form post-subduction porphyry Cu±Mo±Au deposits. Their derivation from partial melting of deep crustal garnet-amphibolites gives these magmas adakite-like high Sr/Y and La/Yb ratios, but they are not formed by slab melting.

Botcharnikov *et al.*, 2011: Nature Geoscience 4: 112–115.
Hildreth & Moorbath, 1988: Contrib. Min. Pet. 98:455–489.
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