## Hydrothermal Dolomitization: a 5-Stage Reaction Sequence Model

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## ABSTRACT

Studies of hydrothermal dolomite (HTD)-hosted gas fields of the northern Appalachian Basin hosted in the Trenton-Black River Group (Keith et al., 2002) have produced an integrative hydrothermal model that may explain the generation, transport, and deposition of anomalous amounts of Mg that characterize HTD and closely analogous Mississippi Valley Type zinc deposits (MVT) deposits.

Applying hydrothermal fluid mineralization theory, derived from extensive practice and experience with hydrothermal fluid mineralization in the economic minerals industry, provides a cross-disciplinary approach to understanding hydrothermal diagenesis in oil and gas reservoirs.

Hydrothermal fluid fractionation and its resulting mineralization is a common process, one affected by both structure and tectonics. It has a much greater effect in petroleum reservoirs than most explorationists have suspected, particularly as related to certain forms of 'diagenesis'. From the minerals point of view, hydrothermal diagenesis is a subset of a much larger system of hydrothermal fluid fractionation. If we understand the fractionation process, we can make predictions about diagenetic porosity development and occlusion.

Hydrothermal fractionation in hydrothermal mineral deposits (e.g. porphyry copper and gold veins) can be viewed as alteration and mineral zoning with respect to deposition from a hot, aqueous fluid. In a given type of metal deposit, compositional suites (mineral assemblages) are deposited in an orderly, predictable sequence that is a function of cooling, depressurization, and the initial composition of the hydrothermal fluid.

Similar processes are may be widely operant in petroleum reservoirs. Much of what has been traditionally interpreted in terms of closed chemical system sedimentary diagenesis (both compactional and burial style) may also be potentially viewed as open-system hydrothermal diagenesis, where much of the reservoir chemistry has been introduced from outside.

In particular, we believe that a certain type of reservoir environment, the aforementioned HTD petroleum deposit type, developed in deep basinal environments (commonly described as basin-centered gas), is especially amenable to a hydrothermal diagenetic approach. In addition, the remainder of

the reservoir chemistry may owe its development to the introduction of exotic chemical components such as halogens (from brine hydrothermal component), carbonate (from bi-carbonate hydrothermal component), vanadium, zinc, magnesium, iron, sulfur, and alkali metals (from hydrolysis and devolatilization of various oceanic materials in sub-basinal basement.

In exploration for economic minerals, large-scale structural controls on fluid fractionation that are the direct result of wrench-faulting have been documented in a number of discovery-related case histories. Specifically, hydrothermal plumes associated with the generation of brines formed at depth follow a curvilinear path as they ascend through the crust to the surface. The specific trajectory of the ascension path is a function of stress trajectories as the hydrothermal fluids move from high-pressure sources to lower-pressure reservoirs.

The reaction sequence model was developed as a hypothetical model for hydrothermal diagenesis of dolomite, but it also can be applied to the understanding of other secondary hydrothermal diagenetic minerals, including clay minerals, silicates, and 'authigenic' feldspars, each of which has its own unique place within a given hydrothermal diagenesis sequence. Significantly, the chemistry for many of these minerals may have been brought to the reservoir by the hydrothermal fluid. As such, much of the reservoir chemistry may not be part of the original reservoir rock.

The hydrothermal dolomitization reaction sequence uses constraints derived from fluid fractionation modeling, transcurrent shear-zone kinematics, geochemistry, and basement structural data.

The stages are:

- 1. Generation of metagenic bicarbonate, halogen-enriched, low pH brines in intracratonic failed rifts or collisional sutures triggered by compressive, convergent orogenesis.
- 2. Low temperature 'passive', fabric-preserving, sucrosic dolomitization of the first replaceable shelf carbonate in the overlying cratonic cover sequence.
- 3. Early saddle dolomitization at or near depositional site; late saddle dolomitization, anhydrite formation, carbon dioxide effervescence, hydrogen loss and possible methane unmixing.
- 4. Sulfide, mainly pyrite, marcasite, and minor sphalerite deposition and hydrocarbon emplacement.

5. Deposition of late calcite at depositional site and illite/smectite/kaolinite clays in and marginal to depositional site. Gas-charged fluids may ascend to shallower reservoirs.

All of the above stages are thought to have occurred in a geologically short time interval, probably less than 5 million years.

Because the fractionation pattern of hydrothermal plumes is regular and predictable, the above pattern of hydrothermal fractionation may be predictable on regional, play and prospect scales.

The 5-stage hydrothermal HTD reaction sequence has substantial physical implications for porosity and permeability development in a reservoir environment. Metasomatic replacement of various facies within shelf limestone environments by sucrosic dolomites in Stage 2 results in the creation of considerable additional void space (13% on a volume basis). Additional void space may be created by hydrothermal dissolution of carbonate materials during the high-temperature Stage 3 formation of saddle or baroque dolomites. In MVT deposits, extensive cave features or collapse breccias may be developed by hydrothermal dynamics during Stage 3. More speculatively, similar large-scale dissolution features may occur in HTD deposits.

The geography of Stage 2 vs. Stage 3 dolomitization is important to reservoir identification. Porosity formed during Stage 2 reaches its maximum extent, then is plugged as Stage 3 ferroan dolomite is deposited. Interface zones between Stage 2 sucrosic dolomites and Stage 3 ferroan dolomites may provide optimal locations for hydrocarbon reservoirs.

Knowledge of the hydrothermal conduit system architecture is critical to the identification of reservoir permeability and porosity. Stage 3 dolomites may be best developed near primary conduits, while Stage 4 sulfides developed in and adjacent to the conduits. Stage 5 calcites, K-rich illites, and K-feldspar may be developed in more distal settings.

As it does in hydrothermal metal deposits, hydrothermal fluid fractionation may leave behind a geochemical footprint in the form of trace metals and other trace elements that can be identified in soil samples collected above the HTD/MVT deposit. In economic mineral exploration, soil sample geochemistry using trace metals has been a productive technique, one which we believe may be successfully applied to petroleum exploration.

In part, this is because new analytical techniques developed over the last few years have allowed us to measure metals in the parts-per-billion range. Another factor, though, is that using hydrothermal fluid fractionation theory, we have a much better understanding of what these data mean.

If the hydrothermal metagenic model is viable, it will have applications from regional to reservoir scale, and it may be possible to predict the most likely location of sweet spots in hydrothermal dolomite plays.