**Subsurface Corrosion of Calcite and Dolomite by Fault-Sourced Hydrothermal Fluids**

**Taury Smith**

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**Abstract**

Porosity in both limestone and dolomite reservoirs can be created and enhanced by fault-sourced hydrothermal fluids. Examples from the Pinda Formation of offshore Angola and the Cogollo Limestone of Venezuela will be used to show a subsurface origin for the dissolution. In the Pinda Formation of offshore Angola, both limestone and dolomite were dissolved in the subsurface. Dolomite (including some saddle dolomite) that formed at temperatures ranging from 65 to 160°C occurs as a cement in some grainstones where the grains are found as intact calcite, partially dissolved and completely dissolved. This dissolution of the calcite is therefore of a subsurface origin. Most of the porosity in some cores and thin sections is of a leached dolomite origin. The fact that the leaching occurred after this high temperature dolomitization confirms a subsurface origin. Hydrothermal fluids rich in H2S are interpreted to have flowed up active faults and into the formation where they were oxidized to create sulfuric acid which did the dissolution. Pyrite and anhydrite precipitation closely follow the dolomite dissolution. This all occurred during early burial prior to oil migration.

In the Cogollo Limestone of Venezuela, there is burial corrosion of limestone reservoirs interpreted to have occurred along strike-slip faults known to have been active during early burial of the formation. The corrosion clearly postdates early near-surface diageneis which is largely cementation and is followed but relatively high temperature dolomite, calcite, and kaolinite precipitation. There would not be a reservoir without this burial corrosion and as a result it is important to drill wells near the faults that were the source for the diageneric fluids. At least three factors make fault-sourced hydrothermal fluids capable of corrosion of limestone: progressive cooling of the fluids, elevated salinity, and increased CO2 in solution. Calcite and CO2 both have retrograde solubility so as fluids cool they become progressively undersaturated and progressively more acidic. pH generally decreases as salinity increases so hypersaline brines coming up faults should be capable of leaching limestone.

Burial corrosion of limestone and dolomite also occur in many other carbonate reservoirs. It can commonly be linked to faults (typically strike slip or transtensional faults) and might therefore be predictable in cases where good seismic data is integrated with good core and petrographic data.
**Selected References**


Subsurface Corrosion of Calcite and Dolomite by Fault-Sourced Hydrothermal Fluids

Taury Smith

Smith Stratigraphic LLC
Introduction

- Dolomitization and leaching of carbonates take place in many different diagenetic environments.
- One environment where these processes occur that has been historically underappreciated is in the fault-controlled hydrothermal realm.
- This is an integrated structural-stratigraphic-diagenetic processes that require some understanding of each of these disciplines.
- Some reservoirs are entirely formed by faulting and hydrothermal fluid flow while others are enhanced or degraded.
The Basics of Hydrothermal Alteration Model

• Hydrothermal alteration occurs when fluids move up active faults and fractures and into formations
• Basement-rooted strike-slip, extensional and especially transtensional faults make best conduits
• If there is a seal or baffle (typically shale or evaporites), upward migrating fluids are forced laterally into uppermost permeable zone
• Alteration can and commonly does take place within a km of surface and probably more likely within 500m
• Fluids can change pressure, temperature, $P_{CO_2}$, pH and salinity in formation on short time scales, all of which can trigger dissolution and precipitation of a range of minerals
Common sites of hydrothermal dolomitization and dissolution
Hydrothermal mineralization and dissolution occur when high-pressure, high temperature fluids move up active faults (most commonly transtensional faults).
Examples of Slave Point Limestone alteration proximal to hydrothermal fluid source at Ladyfern

A: Leached breccia from a heavily altered portion of the 4-26-94-13W6 core. This core represents the most complete stage of alteration of the Slave Point Limestones.


C: Dissolution-enhanced intergranular porosity and saddle dolomite precipitation from a-97-H/94-H-1.

Photomicrograph magnification approximately 10X. Photomicrographs courtesy of Tom Boreen.
Idealized Permeability Evolution of a Fault Zone Modified from Knipe, 1993 and Davies, 2001

Preseismic Period of most hydrothermal alteration

Main Shock and Aftershock Period

Afterslip Period

Creep and Collapse

FLUID FLOW

TIME

Elastic Strain, Microfractures

Fluid flow produces drop in fluid pressure in and around fault zone

Large but very transient dilation.

Pockets of enhanced/persistent dilation at dilation fault jogs and in deformation-induced fracture concentrations at bends and in tip zones.

Aftershocks cluster in tip zones (fault die outs) or at fault bends. These zones become the locations for fluid storage and are the principal sites for mineralization in MVT and other hydrothermal deposits.
Some Reservoir and Pore Types Produced by Hydrothermal Alteration

Dissolution of limestone or dolomite

Vugs, Breccias, Fractures

Matrix dolomite

Leached limestone

Microporosity
Some Indicators of Hydrothermal Alteration

- Saddle dolomite cemented breccias
- Zebra and boxwork fabrics
- Leached dolomites
- Anhydrite and other sulfates
Calcite and Bitumen

Kaolinite and other authigenic clays
Facies Control on Extent of Alteration

Low to Moderate Original Perm

- Only dolomitized around faults
- Breccias and fractures common.
- More alteration on down-thrown side.

High Original Perm

- Strata are pervasively altered far from faults and leached limestone is more likely

Formations that are high-perm throughout may show few obvious signs of hydrothermal alteration.
Fault-Related Hydrothermal Leaching Mechanisms

• Cooling hydrothermal fluids – both calcite and CO$_2$ have retrograde solubility
  – As fluids cool, they can hold progressively more calcite in solution
  – As fluids cool, any CO$_2$ in vapor form will go into solution, dropping the pH and making fluids more aggressive

• Salinity increases and pH commonly decreases with depth – if more acidic brines flow up faults, will be lower pH than \textit{in situ} fluids and capable of leaching

• H$_2$S moves up faults and gets oxidized creating sulfuric acid which has potential to leach limestone and dolomite
Leaching of CaCO$_3$ can occur simply due to cooling fault-derived fluid (modified from Rimstidt, 1997)
Fluids flowing up faults should have higher salinity and lower pH than fluids higher in the section – this could promote leaching.

Heydari, 1997

Hanor, 1993
### Stratigraphic Column with Tectonic Events at Urdaneta West

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- **Andean or Quechua**
  - (Tilt to South)

- **Incaic**
  - (Major Growth of UDW w/ strike-slip)

- **Oregonian**
  - (Reactivation of older faults)

- **Herocynian & Tethyan**
  - (Paleozoic & Jurassic Extensional Faulting)

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**Cogollo Group, Venezuela**

> 1 billion barrels in place in Urdaneta West

**Thanks to Shell Venezuela**
Most leached limestone reservoirs are only microporous in and around where they are leached.
Dissolution occurs in TST in packstones – it’s not meteoric, grainstones completely cemented.

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Dissolution followed by saddle dolomite and kaolinite (dickite?) in oyster packstone of Maraca
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Leaching occurred in facies with best remaining perm at time of alteration.

Leaching by cooling hydrothermal fluids that may have been CO$_2$ charged.
Well locations proposed based on proximity to faults thought to be conduits for leaching fluids.
Leached Limestone from the Natih E reservoir at Al Ghubar Field, Oman

Porosity over 40% in some intervals
Studied Albian Pinda Carbonates

Thanks to Angola LNG
Studied Albian Pinda Carbonates

Iabe Clastics

Pinda

Evaporites

Pre-salt Rift related clastics

Thanks to Angola LNG
Iabe Clastics

Pinda

Evaporites

Pre-salt Rift related clastics

Studied Albian Pinda Carbonates

From R. Blakey website

Thanks to Angola LNG
Study Conducted in Block 2, offshore Angola

Study included 18 cores and cuttings thin sections from ten wells

Made and described hundreds of thin sections

Covered Northern, Central and Southern Fields Areas

- Core studies
- Cuttings Thin Section Studies (some more than 3000 feet of section)
Reservoirs in sandstones and coated grain-oncoid grainstones and rudstones – best carbonate reservoirs are dolomitized and subsequently leached
Dolomite starts out as cement (saddle where large xtals), not as replacement of grains – this dolomite precipitated directly out of supersaturated fluid sourced from fractures– only minor compaction prior to dolomitization suggests shallow burial.
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Evidence for Hydrothermal Dolomitization

- Dolomitization only occurs where basement-rooted faults visible on seismic offset Loeme and cut into Pinda
- Primary fluid inclusions almost all two-phase inclusions with $T_H$ between 65 and 160°C and salinities of 20 wt% - hotter than ambient burial temps at time of dolomitization
- Stable isotopes, strontium isotopes and trace elements all support
- Only minor compaction prior to dolomitization which suggests shallow but hot
- Saddle dolomite in fractures and matrix
Dolomite leaching

- Dolomite leaching is extensive in the Pinda
- It is not reported much in the literature
- The leaching fluids enlarge fractures and are here interpreted to have been sourced from the fractures
- Without dolomite leaching, there might not be fields in some areas
Dolomite leaching occurred in fractures, vugs, and matrix — presence of leaching in fractures suggests fluids flowed up faults and fractures and into matrix.
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Chopa 2 and most other cores showed evidence for strong dolomite leaching.
Hi-Perm

Chopa 1 6982.5

Grainstones variably leached – without leaching, no perm
In some fields, >75% of the porosity appears to be of a leached dolomite origin as it is in this thin section scan.
Dissolution proceeds near the tops of some intervals to the point where super-k zones form.
Pyrite followed by anhydrite is very common in fractures and breccias in the Pinda cores from many fields.

Lombo North 3 10187
Impact of Diagenesis in Pinda – all same rock type – Dolomite is good, too much dolomite (overdolomitization) is bad, leaching is good to really good, anhydrite plugging ranges from OK to really bad.
Leaching interpreted to have been caused by \( \text{H}_2\text{S} \) coming up faults

Either oxidation of \( \text{H}_2\text{S} \) to make sulfuric acid or mixing of two different fluids with varying \( \text{H}_2\text{S} \) composition could make fluids capable of leaching dolomite

Common byproducts of sulfuric acid leaching are \( \text{CaSO}_4 \) (gypsum or anhydrite) and \( \text{FeS} \) (pyrite) (Hill, 1995)

![Graph showing saturation concentration of calcite and dolomite as a function of \( \text{CO}_2 \) or \( \text{H}_2\text{S} \) concentration in volume of dissolved solid per liter. Mixing of two saturated solutions (e.g., A and B) produces an undersaturated solution (C) and renewed aggressiveness. Subsequent dissolution follows line C–D. After Palmer (1991).]
Conclusions

- Carbonate dissolution, or burial corrosion, is a common process in the subsurface.
- It commonly occurs around transtensional faults which when active are conduits for hydrothermal fluids which evolve over time and can produce a range of mineralization and dissolution.