

## **Grain-Edge Dissolution Pores in Carbonates Imaged on Ar-Ion-Milled Surfaces: Authentic or Artifacts?**

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### **ABSTRACT**

Dissolution-related pores around the edges of carbonate grains imaged on Ar-ion-milled surfaces have been documented by several authors. It has been proposed that these pores are related to decarboxylation of kerogen, which produces acids. Alternatively it has been suggested that these grain-edge pores are post-coring artifacts produced at surface conditions. Resolving this issue is important for understanding pore networks and diagenesis in mudrocks.

The artifact dissolution would be related to breakdown of unstable pyrite in the presence of water, which produces acid and sulfate ions. This process is known to take place in some core and on some ion-milled samples as evidenced by the presence of Ca- and Fe-sulfates that result from the reaction. Significant Ca-sulfate (probably gypsum) formation would require dissolution of carbonate grains by the acid, hence the possibility that grain-edge pores are the result.

On ion-milled surfaces, sulfate formation has been observed to be localized primarily in two locations; lining induced microfractures and on pyrite crystals. Most of the microfracture fill forms prior to milling, as typically the gypsum has been milled flat along with the rest of the sample surface. Gypsum is rarely seen to form on carbonate grain surfaces and where it does, grain-edge pores are not present. Casulfate rimming carbonate grains is rarely observed, and where observed formed prior to ion milling.

Grain-edge dissolution pores have been observed around both calcite and dolomite grains. However, only one sample has been found with Mg-sulfate precipitation. Commonly, dissolution is seen around all carbonate grains on any one sample surface. Grain-edge pores vary in morphology. Some grain-edge pores show relatively linear shapes, whereas others are more irregular, and some even show complex, almost dendritic, shapes. In almost all examples, these pores are deeper than they are wide with no bottom being visible. Although most dissolution pore widths are in tens to hundreds of nanometers, in a few examples, carbonate grains show complete or almost complete dissolution. Given that dissolution of carbonate would be necessary for formation of significant amounts of gypsum (which does occur), the question becomes, would the acids on an ion-milled surface preferentially attack edges and form deep pits? Or would dissolution be spread out more evenly across grain surfaces?

Some grain-edge pores show evidence that they distorted the Ar-ion-beam during milling, indicating that they predate the sample surface formation. The apparent depths of grain-edge pores are also more consistent with formation in the subsurface rather than after ion milling. Grain-edge pores are seen in samples that show little or no gypsum formation. Although evidence is not conclusive for all pores, it is probable that most grain-edge pores around carbonate grains result from dissolution in the subsurface.