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Imaging Pores in Sedimentary Rocks: Foundation of Porosity Prediction

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ABSTRACT

This review examines the history and current practice of technologies for imaging of pores in sedimentary rocks. Pores are that portion of the rock volume occupied by components of relative mobility such as water of various salinities, microbial life, petroleum liquids, gases, and supercritical fluids. Through a rock's history the contained pores evolve as the primary detrital assemblage responds chemically and mechanically to changing conditions in the subsurface.

Description and classification of pores based upon their paragenesis depends upon inspection by imaging that allows the pores to be seen and interpreted in the context of historical processes responsible for formation of the pore walls.

Since the late 1960s, sample preparation and imaging methodologies that clarified our understanding of pores in their correct historical context have been at the root of important advances in prediction of porosity and related bulk properties in the subsurface. These older approaches are now joined by new technologies that serve current efforts to extend predictive capabilities to nm-scale pores in the fine-grained, low-permeability rocks that dominate in the deeper parts of sedimentary basins, and indeed, in the sedimentary record as a whole. Placing the smallest pores into their proper paragenetic context presents a challenge in the quest to develop predictive models for porosity evolution in fine-grained rocks.

1.0 INTRODUCTION and BACKGROUND

The term “pore” applied in this review (section 1.1) is underlain by the notion that pores are fundamental rock components that, given a suitable imaging method, one might actually *see*.

Modern concepts of pore interpretation and methodologies of pore imaging grew first from studies of coarser sedimentary rocks, sandstones and limestones, and we begin our paper with an examination of this body of work. We review the technological means, both sample preparation and imaging methodologies, that underpin current models for porosity evolution in sedimentary rocks and that serve efforts to extend this understanding to pore systems in the fine-grained sedimentary rocks known as mudstones or shales. In the second half of the paper we consider specifically the current work on pore imaging in muds and mudstones. In some cases, these smallest sedimentary pore systems may be simple analogues of coarser systems, but in other cases, processes in small pores may depart from significantly from those in coarser systems because of the special chemistry and physics that apply at the nanoscale.

1.1 *What is a pore?*

Pore volume can be considered, most simply, the portion of the total rock volume that is not solid. This viewpoint naturally enables other essential notions: 1. Pores are defined by pore walls. To fully understand the nature of a pore it is essential to discern the character of pore walls; 2. Any particular method of observation (and, indeed, any particular means of bulk measurement) detects only a portion of the total pore population as there are always pores that are blocked from view or too small or too large to be appreciated from a particular image or with a particular method, and, 3. In the Earth’s crust pores are never empty---they are not “voids”, but host components such as water with dissolved solids, petroleum liquids, gases, a mixture of these or, in the deeper subsurface, a supercritical fluid (Fyfe and Thompson, 1978; Strumm and

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4 Morgan, 1996; Tissot and Welte, 1984). Some pores host living organisms (e.g., de la Torre et
5 al., 2003; Kennedy, 1993). Over geologic history pore contents have mobility greater than that of
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7 crystalline or other solid rock components (Goff and Williams, 1987; Morad et al., 2000; Parnell,
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9 1994).

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14 The relative mobility of pore contents is responsible for a fourth and quite interesting
15
16 aspect of pores in sedimentary rocks: the fact that pores change in size, shape, and abundance
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18 over time as the rock's solid and mobile volumes respond to shifting chemical and physical
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20 conditions in the subsurface. For example, movement of pore contents under sediment loading
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22 allows compaction whereas restriction on fluid movement (overpressuring) may retard it.
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24 Transport of dissolved components within the mobile rock volume permits dissolution and
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26 precipitation of mineral volumes that also yield corresponding changes in the pore volume, both
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28 increases and decreases, as pore walls are modified. This paper reviews the various technologies
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30 for observing pores in sedimentary rocks and describes some of the outcomes from visual
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32 inspection of pores and interpretation of pore histories that have led to models for prediction of
33
34 subsurface porosity.
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41 **1.2 *Why look at pores?***

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43 Bulk analysis of porosity and pore size distributions in sediments and sedimentary
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45 rocks is accomplished by several methods, each with advantages and disadvantages (Doveton,
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47 2014; American Petroleum Institute, 1998; Luffel et al., 1996; Pearson, 1999; Schön, 2015; Tiab
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49 and Donaldson, 2015; Van Geet et al., 2000). A key disadvantage to all methods of bulk analysis
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51 relates to the limited manner in which such methods contribute to pore classification. Pores can
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53 be classified by absolute size (e.g., Luxmoore, 1981; Nelson, 2009; Zdravkov et al., 2007)
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55 although a notable challenge concerning the use of size categorization for pores is that an
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4 arbitrary name (e.g., “mesopore”) applied to a given size range may vary across fields of study or
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6 even among different authors in the same field. Pores may also be categorized by relative size
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8 (Etris et al., 1988; Lucia, 1995) and by shape (Desbois et al., 2009; Ehrlich et al., 1991). In
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10 rocks such categories as size and shape pertain only to the final state of a bulk material that may
11
12 have undergone substantial change over a history of mechanical and chemical modification
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14 (Fabricius, 2007; Katsube and Williamson, 1994). The final size (relative or absolute) and shape
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16 of a pore, by themselves, provide only weak clues to the nature and causes of changes
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18 responsible for porosity evolution because a given size or shape may arise by multiple pathways
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20 of modification .
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26 Although bulk measurements of porosity and knowledge of pore size and shape have
27
28 tremendous utility for modeling storage and flow behavior, pore categorization that is not
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30 referenced to the initial geometry of the rock fabric (solids and pores) is inherently handicapped
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32 for assessment of porosity evolution as it lacks information that can be related to timing, mass
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34 transport, and volume changes related to mass transport. Prediction of porosity evolution
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36 depends heavily on understanding of the local material imports and exports that have affected
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38 pore walls of known origins. Pore categorization referenced to the primary detrital framework, a
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40 state against which subsequent change can be measured, has a powerful advantage for use in
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42 porosity prediction and can only be accomplished by inspection.
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48 Compactional strain (volume loss through mechanical pore collapse) is an important rock
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50 modification that can be referenced to the primary depositional framework (Ehrenberg, 1995).
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52 Similarly, assessment of mass-balance, the measure of volume losses and gains affecting the
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54 mineral fraction, requires an understanding of the primary detrital assemblage as a starting point
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56 against which change can be measured (Milliken et al., 1989; Milliken et al., 1994). Whether a
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4 post-depositional precipitate occupies a primary pore versus a secondary pore (no matter the
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6 size) has immense ramifications in terms of the balance of local elemental imports and exports
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8 required. Both pore volume and mineral volumes change during rock history and not always in a
9
10 simple inverse relationship. A mineral (or solid volume) gain does not necessarily result in a pore
11
12 loss if it is preceded or accompanied by a loss in the mineral volume (secondary pore formation).
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15 A mineral (or solid volume) loss does not equate to porosity gain if it is accompanied or
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17 followed by compactional collapse or mineral precipitation. Assessing these complex historical
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19 exchanges between pore and solid volumes depends upon assessment of paragenesis by imaging.
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23 **1.3 Pore categorization based on paragenesis**

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26 *Primary pores* are present at the time of deposition and these can be *intergranular*
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28 (between the detrital particles) or *intragranular* (contained within a particle). Primary
29
30 intergranular pores are the dominant primary pore type within most sandstones and mudrocks
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32 (Figure 1), even after a protracted history of diagenesis (Milliken et al., 2007; Paxton et al.,
33
34 2002; Scholle and Ulmer-Scholle, 2003). Some carbonate sediments and also some mudrocks
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36 contain significant primary intragranular pores (Figure 2) if complex fragments of bioclastic
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38 debris or vesicle-rich pumice are abundant in the grain assemblage (Milliken and Choh, 2011;
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40 Milliken et al., 2007; Scholle and Ulmer-Scholle, 2003) (Figure 1). The primary intragranular
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42 pores within biogenic particles represent spaces formerly filled by the living tissue of the
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44 organism and also structural elements that allowed movement of fluids through the shell wall.
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51 Primary pores, both inter- and intra-granular, are subject to modification by
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53 mechanical and chemical processes in diagenesis. Grain rearrangement and brittle and ductile
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55 grain deformation are microscale mechanical processes that operate to reduce primary pores in
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57 compaction (Chester et al., 2004; Kopf and Behrmann, 1997; Pittman and Larese, 1991); in
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4 carbonate sediments chemical processes may also play a role (Croize et al., 2010). *Cements* are
5 minerals precipitated from aqueous solution (authigenic minerals) into primary pore space
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7 (Milliken, 2003; Milliken and Day-Stirrat, 2013). Organic matter of diagenetic origin (residual
8 hydrocarbon) can fill pores in a manner analogous to cement (e.g., Huc et al., 2000; Moller and
9 Friis, 1999).

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16 *Secondary pores* form after deposition, mostly through dissolution of the primary detrital
17 grains or, less commonly, through dissolution of diagenetic elements such as cements and grain
18 replacements (e.g., McBride, 1977; Pettijohn, 1941; Schmidt and McDonald, 1979a) (Figure 3).
19
20 Fracture pores are a type of secondary pore, and thus, both mechanical and chemical processes
21 influence the formation of secondary pores. Terminology for secondary pores is complex and
22 relates to spatial occurrence of the pore relative to the detrital framework (e.g., intragranular
23 secondary pores, moldic pores, oversize pores) or the larger-scale fabric of the rock (e.g.,
24 fracture pores of intragranular, transgranular, or circumgranular types). Fracture pores arise from
25 breakage and separation of the solid rock volume. Simple intragranular fracture pores clearly
26 arise from a redistribution of the primary porosity (Makowitz and Milliken, 2003), but the
27 derivation of the space within most through-going transgranular fractures is generally unclear.
28
29 The relative timing of pore modifications relative to deformation (Laubach et al., 2010; Laubach
30 and Milliken, 1996) also factors into the terminology for cements and grain replacements (e.g.,
31 synkinematic cements). An alternative mechanism of secondary pore development, and one of
32 considerable current interest in research, relates to processes that occur during thermal
33 maturation, for example by gas bubble formation or by volume loss from organic matter
34 (kerogen or residual hydrocarbons) during thermal cracking (Loucks et al., 2009).
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4 *Grain replacement* denotes authigenic minerals precipitated within a space formerly
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6 occupied by a dissolved grain, regardless of the relative timing between dissolution and
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8 precipitation (Milliken, 2003). Ascertaining the timing between grain dissolution and mineral
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10 precipitation within the resulting secondary pore is one of the greatest challenges in paragenetic
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12 assessment. Grain replacements seldom share the precise mineralogy of the dissolved grains and
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14 the elemental imbalances thus imposed have to be satisfied by elemental imports and exports that
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16 require aqueous transport (e.g., Fedo et al., 1997; Milliken, 2004; Milliken et al., 1994;
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18 Nedkvitne et al., 1993; Wolela and Gierlowski-Kordesch, 2007). Replacement may occur nearly
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20 synchronous with dissolution across interfaces that represent only the smallest of fluid films
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22 (Merino et al., 1993), or, alternatively, may occur long after grain dissolution and within
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24 macroscopic pores that existed for a prolonged period before being filled. The petrographic
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26 means to discriminate the above scenarios are unclear in many cases, but the fact that most grain
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28 replacements are accompanied by intergranular cements of the same composition (Milliken,
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30 1989) argues that secondary pores provided sites for cement nucleation essentially equivalent to
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32 sites in intergranular pores (Milliken, 2003). Complete filling of secondary pores is unlikely in
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34 such a situation and this type of replacement is associated with much preserved secondary
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36 porosity. Situations in which grain replacements display a preferential localization on dissolved
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38 grains (e.g., Milliken 2003) argue for a tighter association between dissolution and precipitation
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40 (Maliva and Siever, 1988) with little or no associated secondary pore development (Figure 4).
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42 Processes of pore modification through cementation, dissolution, and grain replacement can be
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44 so profound as to impart a complete inversion of the pore distribution, what was once solid
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46 material becoming pore while what was once pore becomes solid (Figure 5).
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Grain replacements in particular cause loss of information on pore paragenesis as diagenetic modification becomes extreme. As mentioned above, because grain replacements are precipitates from an aqueous solution that fills the pores, they are typically accompanied by cements of similar composition and timing (Milliken, 1989). If the growth of authigenic minerals as simultaneous grain replacements and cements becomes pervasive and large, the grain/intergrain fabric that defines sedimentary materials can be erased (Figure 6). In such a case it becomes necessary to characterize pores as “intercrystalline”, “intracrystalline”, or, perhaps, “fracture-fill” without reference to the context of the original grain framework. Such pores dominate within rocks that have lost their sedimentary fabrics during metamorphism but also within rocks such as crystalline dolomites that are still generally considered sedimentary (e.g., Machel and Anderson, 1989; Murray, 1960). Assessment of the timing and mechanisms of processes responsible for such pores is extremely challenging because mass exchanges cannot be related to a known primary detrital framework.

2.0 Historical Context: Pore Imaging in Sandstones for Conventional Reservoir Characterization

Use of impregnation media for the stabilization of friable specimens prior to thin section preparation is a technique dating to the late 19th century (Wilkinson, 1900). Addition of color to the impregnation material was done in the 1940s (Lockwood, 1950) and perhaps earlier, although this technique did not become widely practiced and commercially available until the late 1960s. The idea behind colored impregnation media (typically some type of plastic resin) is to inject rock pores with the colored medium prior to thin sectioning, such that natural pores appear in a distinctive color whereas pores created by mechanical damage during cutting,

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4 grinding, and polishing the section are filled only with the clear adhesive used to attach the rock
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6 slice to the supporting glass slide (Figure 7).
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9 In the late 1960s to mid-1970s widespread application of this simple technology for
10 coloring pores prior to visual observation, brought about a radical transformation in the
11 understanding of pore evolution as the widespread occurrence of secondary pores within former
12 grain volume was recognized (Hayes, 1979; Lindquist, 1977; McBride, 1977; Pittman, 1979;
13 Schmidt and McDonald, 1979b; Stanton, 1977), confirming and expanding upon the earlier
14 observations of Pettijohn (1941). Prior to application of colored impregnation media, direct
15 observations pores and the evolution of pores were rarely mentioned and work on porosity
16 evolution focused mostly on experimental approaches (Allen and Chilingarian, 1975; Maxwell,
17 1960) and modeling of porosity assessed through bulk, and often, indirect, measurements such as
18 bulk density, velocity, or log-derived porosity (Athy, 1930; Weller, 1959). An exception is the
19 work by Taylor (1950) that approached the problem by examining grain contacts, thereby
20 cleverly avoiding the necessity of measuring the porosity. By the 1970s, however, the
21 availability of colored impregnation media had fostered development of a complex terminology
22 for pore description (as described above) and novel approaches to quantitative partitioning of
23 total porosity across specific pore types through the use of imaging data. A key discovery was
24 that total porosity as determined by bulk measurement is an unsuitable proxy for intergranular
25 space. To quantify the role of compaction in subsurface porosity decline it is necessary to use
26 observational methods that account for the primary intragranular pores within grains, the filling
27 of intergranular pores by mineral precipitates (cements), and the generation of secondary pores.
28 Following soon upon this development research laboratories at major oil companies, hoping to
29 develop empirical methodologies for reservoir quality prediction (e.g., papers in Wilson, 1994)
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4 amassed large petrographic databases for sandstones. An important development arising from
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6 this data collection effort was the concept of intergranular volume (IGV, Paxton et al., 2002;
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8 Szabo and Paxton, 1991).

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11 (1) $IGV = \text{intergranular pore space} + \text{intergranular cement} + (\text{detrital matrix})$

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14 all parameters expressed as a percent of total rock volume

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16 In older literature IGV is also known as the “minus-cement porosity” or the “pre-cement
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18 porosity”. Of key importance is the omission of both primary intragranular and secondary
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20 intragranular pores from IGV.

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23 Application of equations denoting compactional change referenced to the initial sediment
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25 bulk volume (compactional porosity loss, COPL; Ehrenberg, 1989):

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28 (2) $COPL = P_i - (((100 - P_i) * IGV) / (100 - IGV))$

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31 where P_i is the initial intergranular porosity and all parameters are expressed as a percent
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33 of total rock volume

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36 led to the recognition of compaction as the dominant cause of subsurface porosity decline in
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38 sandstones (Lundegard, 1992). Because visualization of mineral components in rocks is readily
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40 accomplished, cementation has long been recognized as a factor in porosity decline in sandstones
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42 (Fothergill, 1955; Gilbert, 1949; Goldstein, 1948; Johnson, 1920; Lerbekmo, 1961). Because
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44 compaction and cementation operate in concert however, a quantitative understanding of
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46 cementation did not advance until the role of compaction was clarified and isolated as described
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48 above. Cementational porosity loss (CEPL) can also be referenced to the initial sediment volume
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50 (Ehrenberg, 1989; Lundegard, 1992):

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53 (3) $CEPL = (P_i - COPL) * (C / IGV)$

Where C is the volume of intergranular cement and all parameters are expressed as a percent of total rock volume.

COPL and CEPL observed in large petrographic data sets for sandstones (Lundegard, 1992) established that compaction is the dominant cause of porosity decline in the subsurface. The wide variation in these parameters led next to the recognition that the composition of the primary detrital grain assemblage exerts a strong control on the progress of compaction, a concept that was verified by observation (Smosna, 1989) and experiment (Pittman and Larese, 1991). Sandstones that contain an abundance of ductile grains (typically fine-grained lithic fragments of sedimentary, volcanic, or metamorphic origin) may lose almost all intergranular pore space to compaction whereas sandstones composed dominantly of rigid grains (quartz and feldspar) follow a different pathway of compactional strain (Pittman and Larese, 1991). In either case, compaction can be modeled as an exponential curve with the rate of decline with effective stress adjusted to reflect the behavior of the ductile and rigid grains in the overall grain assemblage (Lander and Walderhaug, 1999).

Recognition that rigid-grain sand packs achieve compactional stabilization at an IGV of around 26% at a depth of 1.5 to 2.0 km further established that intergranular porosity values below 26% in such a grain pack must arise by cementation (Paxton et al., 2002).

Attempts to model the progress of pore loss through cementation, in particular quartz cementation, have benefited from another imaging technology, cathodoluminescence, which can be performed on both light-microscope and electron-microscope systems. The early work of (Sippel, 1968) showed that many apparently sutured contacts between adjacent quartz grains were in fact compromise growth boundaries between cement crystals nucleated on opposing pore walls. With the advent of SEM-based CL systems in the early 1990s Sippel's observations were

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4 widely confirmed and the previously popular pressure solution model (de Boer, 1977; Lehner,
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6 1995) was largely abandoned as an explanation of porosity decline in sedimentary basins. At
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8 about the same time systematic study of deep sedimentary basins having simple burial histories
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10 (e.g., Land et al., 1987) and exacting fluid inclusion work on zoned quartz cements
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12 (Walderhaug, 1994, 1996) elucidated the strong thermal controls on the growth of quartz cement,
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14 leading to integrated models for compaction and cementation of great practical efficacy
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16 (Ajdukiewicz and Lander, 2010). Today pore-scale reservoir quality is modeled using
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18 empirically calibrated kinetic approaches that yield a fairly tight envelope of prediction (Taylor
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20 et al., 2004; Taylor et al., 2010; Taylor et al., 2015; Tobin et al., 2010).

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26 A key point is that an understanding of paragenesis, founded upon imaging, was at the
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28 root of this predictive understanding of subsurface sandstone porosity. Technologies such as
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30 colored impregnation media and cathodoluminescence imaging revealed the processes that
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32 control porosity evolution (compaction and cementation) and a fostered a quantitative
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34 assessment of the progressive outcomes of those processes operating in the subsurface. In turn,
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36 models founded upon a correct understanding of process achieved great accuracy and precision
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38 in prediction (Taylor et al., 2004; Taylor et al., 2010; Taylor et al., 2015; Tobin et al., 2010)..
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41 The following sections of this paper examine current technologies for imaging of pores in
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43 sedimentary rocks, with particular emphasis on mudrocks and the quest to derive a predictive
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45 understanding of porosity evolution in the Earth's most abundant sedimentary materials. Imaging
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47 of the extremely small components in mudrocks at a scale appropriate to evaluating the processes
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49 affecting those components has only recently become widely available to the geoscience
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51 community that is interested in predicting mudrock properties and further advances in
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53 observational science are needed before process-based prediction models can be devised.
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3.0 Imaging methods for sedimentary rocks

The currently available toolkit for imaging sedimentary rocks is extensive (Table 1). The light microscopy that was available from the middle of the 19th century (Folk, 1965; Summerson, 1976) has been joined by a wide array of imaging techniques based upon interactions between specimens and energized probes. Short-wavelength light, laser light, electrons, X-rays, neutrons, ions of various charge and weight, and acoustic and mechanical energy are some of the options beyond visible light that are available for investigating rock components and fabrics. The direct interaction of energetic probes with the material forms the basis of some methodologies and signals secondarily generated by the interaction also can be detected, leading to the great variety of imaging tools listed in Table 1. Some methods, such as back-scattered electron imaging, are broadly applicable to the full range of materials that are commonly found in sedimentary rocks where as other tools, are most useful with respect to some narrower range of material such as organic matter (e.g., CARS) or a subset of mineral components (e.g. CL).

All imaging methods have a characteristic upper and lower limit to their operating magnification and it is important to note that the theoretical maximum resolutions may not be readily achieved in routine imaging efforts. Finally, methods that are optimized to provide information on pores, pore sizes, and pore-size distributions, especially at very small scales, are not in many cases the best methods for understanding the composition and historical context of the pore walls and vice versa. For example, the electron beam energies required to generate signals for X-ray elemental mapping (EDS and WDS) create beam widths and interaction volumes within the specimen that are not compatible with imaging resolutions sufficient to see pores in mudrocks. Obtaining imaging information on size, shape, and composition on mineral, organic matter, and pore components necessarily requires application of multiple methodologies

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4 across a variety of scales. Techniques highlighted in red Table 1 are ones that offer both high
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6 spatial resolutions and compositional information that potentially can advance our understanding
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8 of pore paragenesis at the nanoscale.
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11 Careful sample preparation is crucial for obtaining meaningful results from any imaging
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13 method. It is important to understand the limitations of any preparation method as well as
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15 potential preparation-related artifacts which can lead to misinterpretation of the imaging or
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17 analysis results. In addition, it is important to consider how a specific sample preparation fits
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19 into the imaging workflow when multiple imaging technologies are employed so as not to
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21 interfere with subsequent measurements. For many micro- and nano-porous rock samples,
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23 simple mechanical polishing such as used for optical thin sections of coarser grained materials is
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25 too coarse of a method to see the smallest pores because artifacts from mechanical damage in
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27 polishing (holes from pitting and plucking) are similar in scale to natural pores. To overcome
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29 this, ion milling (Heaney et al., 2001) is utilized to create the highly polished surface with
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31 minimal artifacts that is necessary for SEM, TEM, STEM, EDS, EELS, and CL (Loucks et al.,
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33 2009; Sondergeld et al., 2010b). There are two types of ion milling: Broad Ion Beam (BIB)
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35 which typically utilizes argon ions and Focused Ion Beam (FIB) imaging which typically utilizes
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37 gallium ions. BIB is preferred for most 2D SEM imaging and analysis of sedimentary rocks
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39 because of the relatively large area, upwards of an inch diameter, that can be milled in a few
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41 hours, provided sufficient mechanical polishing of the sample has been done beforehand (Curtis
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43 et al., 2014; Goergen et al., 2014). FIB (Figure 8) is primarily reserved for 3D FIB-SEM and
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45 TEM sample preparation because of the relatively small area that can be milled in a given time.
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47 The FIB is well suited for these imaging methods in that it can be mounted on the same sample
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49 chamber as the SEM for imaging purposes and the focus and position of the ion beam can be
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controlled for precision milling. The two artifacts that are a common concern for any ion milled sample are curtaining artifacts (Figure 8C) and sputter-redeposition (Figure 8D) (Phaneuf, 2005). One should also be aware of beam damage to sensitive structures,, as this is often is a problem in TEM in the form of the generation of an amorphous layer (Phaneuf, 2005). Milling artifacts can be mitigated with proper care in choosing sample position, milling times, and energies of the ion beam. .

4.0 Current research: Imaging pores in fine-grained sedimentary rocks

4.1 Challenge: Imaging very small pores

Fine-grained sedimentary rocks (known as mudstones, mudrocks, or shales) have the same range of primary and secondary pore types as observed in sandstones and limestones, as least insofar as can be determined from pores that can be imaged (Gale et al., 2014; Krinsley et al., 1998; Milliken, 1992; Milliken and Day-Stirrat, 2013; O'Brien and Slatt, 1990) (Figure 9).

Typically, the largest pores in fine-grained sediments are those associated with primary intragranular spaces within intact skeletal grains, but such pores tend to have localized distributions. Primary intergranular pores in lithified mudrocks tend to be filled with cement (see next section). Fracture pores (Figure 9C) may constitute some of the largest pores present in lithified mudrocks (Gale et al., 2014), however further research is needed into the quantitative contributions of fracture pores to the total pore system. Few fracture pores are encountered at the scale of imaging required to view the dominant intergranular and secondary pores in mudrocks (Gale et al., 2014).

The dominant intergranular pores in muds are intrinsically small. The high porosity that characterizes fine-grained sediments at deposition (up to 80 percent) is diminished by compaction within the first few meters of burial (e.g., Bartholdy et al., 2010; Velde, 1996), but

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4 porosities in the range of 30-40 percent remains even at depths of around 1 km (Day-Stirrat et
5 al., 2012; Velde, 1996). In this early stage of burial, intergranular pores in muds are generally no
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7 larger than a micrometer at even at shallow burial depths of a few meters below the seafloor
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9 (Figure 9A). The largest intergranular pores in the early compaction of mud are typically
10
11 affiliated with packing flaws and sheltered spaces immediately adjacent to silt particles (Day-
12
13 Stirrat et al., 2010; Desbois et al., 2009; Milliken and Reed, 2010; Oertel, 1983; Schneider et al.,
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15 2011). The intergranular pores interstitial to clay-size particles are exceeding small, generally
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17 measured in nm or tens of nm (Desbois et al., 2009; Milliken and Reed, 2010).
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24 At early stages of burial, in muds with porosity in the range of 40-60 percent, SEM-
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26 determined porosity matches closes the porosity measured by adsorption or other bulk methods
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28 (Nole et al., in review). However, in mudrocks that have undergone considerable compaction and
29
30 cementation much of the total porosity (as much as 70 to 90 percent) is not detected by SEM
31
32 imaging (Keller et al., 2011a; Keller et al., 2011b; Milliken et al., 2013). Many mudrocks that
33
34 have experienced a protracted history of diagenesis lose even the pores in the range of 10s to
35
36 100s of nm (Milliken et al., 2013). Pores in the range of 2 nm size or smaller overlap the size of
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38 spaces related to crystal site vacancies and other crystal defects, intercrystalline spaces within
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40 clay minerals and zeolites, and crystal boundary fluid films, all features that, historically,
41
42 generally have not been considered as part of the porosity. If such small spaces host mobile
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44 phases such as water or gases, however, these small spaces are detected as pores from the
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46 perspective of many forms of bulk analysis (e.g., NMR) and also by imaging at the highest
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48 available, but not widely applied, TEM and HIM resolutions (Table 2). There remains great
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50 uncertainty as to the genetic classification of the smallest pores (< 100 nm): Are the smallest
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52 pores primary intergranular pores, intragranular pores inherited from the source rock, or
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secondary pores relating to post-depositional processes that have mobilized the grain volume into the pore fluid? Answering such questions depends upon methods of imaging that provide some information on the composition of the solids that constitute the pore walls (Figure 10).

4.2 Challenge: Imaging very small cement crystals

A key knowledge gap related to porosity prediction in fine-grained sediments is that the IGV concept has yet to be refined for these materials, the principle obstacle being a lack of information about the progress of cementation (Giles et al., 1998; Milliken and Day-Stirrat, 2013). The literature contains an abundance of porosity decline curves for fine-grained sediments over depth ranges from the surface to 5 km of burial (reviewed by Mondol et al., 2007), the greater number of which are based on proxy measurements (e.g., density or velocity). Such values for porosity decline cannot be applied as compaction curves until the role of cementation is assessed.

The greatest challenge to assessing cementation in muds, of course, is that, as described above, the pore spaces available for cement emplacement are generally quite small. Thus, pursuit of cement studies in fine-grained sediments requires high-resolution imaging methods. The rare larger pores found locally within skeletal fragments or fractures present a window for assessing the processes that potentially affect smaller pores (Figure 11; further examples provided in Milliken and Day-Stirrat, 2013, their Figure 5, p. 14), but do not fully confirm the nature of processes operative in the smallest pores.

Quantitative assessment of cements within mudrock pores requires imaging methods that not only resolve the pores and pore-fills at submicrometer scales and but also provide

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4 compositional information that allows discrimination of pore walls made of primary (grain)
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6 versus secondary (cement, grain replacement, or residual hydrocarbon) components.
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9 X-ray mapping by EDS and cathodoluminescence are key methodologies for
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11 compositional imaging but have resolution limits that are not fully satisfactory for observing
12
13 cements in mudrocks (Figure 10). Sample preparation methods that yield sample thinness
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15 smaller than interaction volumes for X-ray and CL generation may extend the utility of these
16
17 methods for cement inspection. Imaging techniques such as TEM and HIM that provide ready
18
19 access into magnifications that reveal the smallest pores have not been extensively integrated
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21 with compositional information, for example from EELS. Techniques such as charge contrast
22
23 imaging (Watt et al., 2000), nano-SIMS (Elphick et al., 1991), and SXRF (Pushie et al., 2014)
24
25 may also assist cement characterization at very small sizes.
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31 *4.3 Challenge: Imaging across scales*

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33 Another challenge for assessing porosity evolution in fine grained systems concerns the
34
35 careful integration of imaging observations across scale because at the size of the smallest pores
36
37 it becomes quite difficult to assess the nature of the surrounding materials (grains, cements, grain
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39 replacements, detrital organic matter, or diagenetic organic matter). In mudrocks, in almost every
40
41 case, crystals are larger than associated pores, and this contrast becomes relatively greater for the
42
43 smallest pores. Thus, it is intrinsically difficult to characterize both pores and crystals at a single
44
45 imaging magnification. Keeping track of the identity of particular crystals and other solid
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47 materials (kerogen and residual hydrocarbons) while applying the imaging scales appropriate for
48
49 characterization of associated pores is one of the central challenges of small pore
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51 characterization. Benefits of the highest resolution imaging will be easiest to gain if samples are
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53 placed through a sequence of inspection steps, beginning with light microscopy and then moving
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4 through more conventional SEM-based approaches before higher-resolution techniques such as
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6 HAADF, SANS, or SAXS are attempted. Performing imaging across such a range of scales will
7
8 inevitably confront issues of conflicting sample preparation requirements. Detailed knowledge of
9
10 sample heterogeneity across a range of scales, even if it cannot be gleaned entirely from a single
11
12 field of view, will provide vital context for the paragenetic classification of pores that will serve
13
14 the goals of pore prediction. Imaging techniques that provide both high-resolution and
15
16 compositional information (e.g., EELS, HAADF, SANS, SAXS, SXRF) are of special interest.
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18 Efforts to extend the reach of compositional imaging methods such as BSE, EDS, and CL to
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20 finer scales are particularly worthy of research attention.
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25 26 *4.4 Challenge: Possible contrasts of porosity evolution in finer versus coarser sediments*

27 28 4.4.1 Compaction

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30 Both observation (Day-Stirrat et al., 2012; Milliken and Reed, 2010; Yang and Aplin,
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32 2007) and experiment (Dewhurst and Aplin, 1999; Emmanuel and Day-Stirrat, 2012; Mondol et
33
34 al., 2007; Schneider et al., 2011) show that pore loss in mudrock compaction is size-dependent,
35
36 larger pores being more easily collapsed in response to effective stress. The smallest size range
37
38 of pores (<100 nm) seem especially resistant to mechanical collapse (Dewhurst and Aplin, 1999;
39
40 Emmanuel and Day-Stirrat, 2012). Mudstones that have undergone a protracted history of
41
42 diagenesis have very low porosities and modal pore sizes in the range of a few nm (Aplin et al.,
43
44 2006; Katsube and Williamson, 1994; Milliken et al., 2012). The small modal pore sizes
45
46 (generally less than 4 nm) in organic matter-hosted pore systems (Milliken et al., 2013) suggests
47
48 that these may be residual pore populations that remain because frictional forces acting on
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50 bubbles of very small size are too great to allow them to migrate under compactional loading
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52 (Brown, 2000).
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4 Between the porosity range of 30 to 50% observed in mudrocks buried less than about a
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6 kilometer (also the typical porosity range achieved in experimental compaction studies) and
7
8 porosities below 10% observed in mudrocks with more extensive diagenesis (typical of oil and
9
10 gas shales) there is a considerable gap in our understanding of the mechanisms that drive
11
12 porosity decline. Compactional stabilization of rigid sand grain packs leads to the conclusion that
13
14 cementation is the dominant mechanism of porosity decline in sandstones at depths greater than
15
16 1.5 to 2.0 kilometers (Paxton et al., 2002), but whether there is an analogous depth of
17
18 compactional stabilization in muddy sediments is unknown.
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24 As mentioned in the preceding review of sandstone porosity prediction, grain
25
26 composition is a major control on the compactional path. Compositional variety of grain
27
28 assemblages in fine-grained sediments is large, spanning the full range of what is observed in
29
30 sandstones and limestones with the addition of the substantial detrital clay mineral content
31
32 (Milliken, 2014). That fine-grained grain assemblages should display a similar variety of
33
34 compactional response across compositional variation seems a plausible hypothesis but this idea
35
36 has not been fully tested.
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41 Experimental work on compactional response of siliciclastic muds having different
42
43 silt/clay ratios (Day-Stirrat et al., 2012; Dewhurst and Aplin, 1999; Schneider et al., 2011)
44
45 demonstrate the control of grain sorting on packing flaws that lead to higher porosity and
46
47 permeability in siltier grain mixtures. However, the impact of differing mineralogical
48
49 compositions of the silt- and clay-size particles, for example the response of carbonate-rich
50
51 sediments versus siliciclastic ones, or inorganic versus biogenic sediments, has not been
52
53 explored. It is also expected that grain assemblage composition will affect the path of
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55 cementation because grains of different composition differ widely in chemical reactivity and this
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4 in turn may further modify compaction. Fine-grained assemblages that are rich in biogenic
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6 carbonate and opal and also volcanogenic grains may be prone to early cementation that
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8 substantially inhibits compaction (Aplin and Macquaker, 2011; Macquaker et al., 2014; Milliken,
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10 2014).
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14 To date, efforts to apply quantitative IGV measurement and porosity decline
15
16 assessment (equations 1-3) in rocks other than sandstones been limited (e.g., Budd, 2002; Melzer
17
18 and Budd, 2008) and this relates in part to the challenges of imaging very small pores and pore
19
20 fills as described above. Another challenge for compaction modeling is the presence of abundant
21
22 primary intragranular pores in some mudrocks. If the primary intragranular volume in mudrocks
23
24 is subject to the same compactional reduction as intergranular pores (an assumption that needs to
25
26 be tested) a similar numerical approach to measuring compactional strain might be applied in
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28 limestones and mudrocks that contain abundant primary intragranular pores. In such an approach
29
30 the total primary porosity (primary intergranular porosity plus primary intragranular porosity)
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32 could be substituted for IGV and a cement value that includes intragranular cement can be
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34 substituted for intergranular cement, assuming the primary versus secondary origin of the
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36 intragranular space can be determined.
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43 4.4.2 Cementation 44

45 Theoretical reasons can be raised to support contradictory ideas about cementation in
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47 mudrocks. On one side it can be postulated that mudrocks may be more prone to cementation
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49 than coarser sediments because in some cases they contain highly reactive grain assemblages that
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51 provide abundant solutes that lead to precipitation (Milliken, 2014) and also because their very
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53 fine constituent particles provide ample surface area to favor nucleation.
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4 However, at least three lines of reasoning, encompassing the operation of crystal
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6 nucleation and growth rates, suggest that mineral precipitation within mudrocks may be inhibited
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8 relative to precipitation within larger pores of sandstones and limestones.
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11 First, it is clear from observations in sandstones that nucleation of authigenic minerals
12
13 from pore-filling aqueous solutions is heterogeneous. Cement nucleation in sandstones in all
14
15 cases takes place on pre-existing mineral surfaces (pore walls). For particular mineral systems
16
17 such as quartz (Heald and Larese, 1974), albite (Kastner and Siever, 1979), and ankerite (Gale et
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19 al., 2010; Loomis and Crossey, 1997) nucleation and crystal growth require specific mineral
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21 substrates. Where such substrates are covered by detrital or diagenetic coatings precipitation of
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23 such minerals is strongly inhibited (Heald and Larese, 1974). Quartz and albite precipitation
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25 seem to be inhibited even in the presence of supersaturated solutions (Land and Macpherson,
26
27 1992). In mudrocks, surfaces amenable to nucleation of quartz and feldspar are reduced because
28
29 clay-size, detrital clay-minerals and other materials such as ductile kerogen and residual
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31 hydrocarbons effectively coat surfaces that would otherwise provide nucleation sites (Figure 9).
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38 Even in the case that small nucleation sites are available in nano-porous systems, a
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40 further possible limitation to cement nucleation and growth concerns the size of the critical
41
42 nucleus for sustained crystal growth. At the scale of nm to a few microns the interfacial energies
43
44 of small crystals impose a significant limitation on crystal stabilities in solution (e.g., Ehrenberg
45
46 and Walderhaug, 2015; Emmanuel et al., 2010). In sandstones, pores smaller than 10 μm
47
48 manifest inhibited quartz cement growth compared to associated larger pores (Emmanuel et al,
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50 2010), an observation that has strong implications for the order-of-magnitude smaller pores that
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52 dominate in mudrocks.
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4 Finally, observations in sandstones show a counter-intuitive negative correlation between
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6 the grain size of detrital quartz (and total surface area) and quartz cement growth (Lander et al.,
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8 2008; Makowitz and Sibley, 2001). The slower growing crystal faces that ultimately dominate
9
10 are expressed more quickly in smaller crystals, thus imposing slower overall rates on smaller
11
12 nucleation substrates and lesser ultimate cement volumes (Lander et al., 2008). This
13
14 crystallographically controlled growth that leads to cement thickness variations, evident in grain
15
16 populations of sand-size ($> 62.5 \mu\text{m} - 2.0 \text{ mm}$), is expected to be even more strongly manifest on
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18 quartz particles of coarse clay- to silt-size ($1 \mu\text{m} - 62.5 \mu\text{m}$). It is possible however that available
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20 pores in mudrocks are so small that growing crystals may contact the pore walls before crystal
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22 growth rates are slowed by development of euhedral faces (Lander and Laubach, 2015).
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31 *4.5 Challenge: Placing organic matter components into paragenetic context*

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33 Recent interest in unconventional resources has brought considerable attention to
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35 organic-rich mudrocks (Howarth et al., 2011; Jarvie et al., 2007; Montgomery et al., 2005;
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37 Passey et al., 2010; Sondergeld et al., 2010a). New techniques for sample preparation by Ar-ion
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39 cross-section polishing (described above; Loucks et al., 2009) allowed more confident
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41 interpretation of mudrock pores that were ambiguous in samples prepared as broken surfaces or
42
43 by mechanical polishing (Figure 8A and B) and application of this technique reveals that the OM
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45 component hosts an important portion of the total porosity in some mudrocks (Loucks et al.,
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47 2009; Milliken et al., 2013; Passey et al., 2010). Examination of OM-hosted pores using SEM
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49 techniques has naturally led to the examination of the OM itself (e.g., Bernard et al., 2012b;
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51 Fishman et al., 2012) and work is on-going to reconcile these small-scale observations to the
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53 larger body of organic petrology that is based on reflected light microscopy (Stach and al., 1982)
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4 and organic geochemistry (Tissot and Welte, 1984). Petrographically, is clear that some OM is
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6 part of the detrital grain assemblage and may contain primary intragranular pores whereas OM
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8 may also be an authigenic component (bitumen, solid bitumen, residual hydrocarbon,
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10 pyrobitumen, etc.) that fills primary porosity (Loucks and Reed, 2014; Milliken et al., 2014).
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12 Both detrital and authigenic OM can develop secondary pores (Loucks and Reed, 2014). These
13
14 different classes of OM (detrital and authigenic) constitute widely varying proportions of the
15
16 total organic content (TOC) of mudstones (Bernard et al., 2012b; Fishman et al., 2012; Loucks
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18 and Reed, 2014; Milliken, 2014; Milliken et al., 2014), and this variation calls into question the
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20 degree to which a bulk measure of TOC can be used to identify OM-rich mudrocks that are
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22 purely hydrocarbon sources versus ones that simply contain migrated hydrocarbons versus ones
23
24 that host a mixed detrital and diagenetic organic component. Work to clarify the
25
26 pressure/temperature controls on porosity evolution within OM of different types is ongoing.
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28 Imaging methods that reveal compositional variations related to OM type (CARS, EELS, SAX,
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30 SANS) are of great interest in this area of research.
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41 **5.0 Concluding remarks**

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43 For sedimentary rocks in general, the range of pore sizes that is typically present requires
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45 multiple imaging methods to investigate pores across contrasting scales. The nanoscale size of
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47 pores in mudrocks in particular necessitates imaging methods alternative to those typically used
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49 for other sedimentary rocks.
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53 In the fine-grained sedimentary systems that are of interest for unconventional resources,
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55 much work remains to be done in terms of placing pores into the context of rock history in a
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57 manner that that support efforts at prediction It is clear that pore systems in mudrocks undergo
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4 dramatic alteration in diagenesis, but the basic mechanisms of this modification are not fully
5
6 understood. Although the basic categories of pores in fine-grained rocks (primary, secondary,
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8 inter-, intra-granular) are fully analogous to pores in coarser grained lithologies, porosity
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10 evolution in mud and mudrocks may follow rather different pathways as a consequence of the
11
12 peculiarities of chemical and mechanical processes as expressed at the nanoscale.
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19 In conventional reservoirs new ways of seeing pores and pore walls (colored
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21 impregnation, CL-imaging) opened new avenues for quantification that allowed the driving
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23 processes of porosity evolution to be modeled accurately. The ability to recognize the meaning
24
25 and significance of novel observations made with new techniques (e.g., CL) depended greatly
26
27 upon the store of knowledge and insight built up from application of previous methods (e.g.,
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29 light microscopy) as no one method holds the key to full understanding. In the fine-grained
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31 systems that now draw our attention, empirical understanding is still being built and the fine
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33 crystal sizes and compositional complexity of these rocks require techniques to gather
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35 observations across a range of scales from the millimeters to nanometers. Knowledge and use of
36
37 the techniques and approaches described in our review will allow researchers to elucidate the
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39 chemical and mechanical controls on porosity evolution in a way that, we hope, can ultimately
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41 lead to useful powers of prediction for porosity and related bulk rock properties in fine-grained
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43 sedimentary rocks.
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Figures

Figure 1. Primary intergranular pores and intergranular volume (IGV).

- A. Quartz-rich sandstone with quartz cement and preserved primary intergranular pores which are filled with a blue plastic resin. Oligocene, France. Plane-polarized light image modified from Milliken et al. (2007).
- B. Interpreted view of image A. Surviving intergranular pores are dark blue; pale blue mask cover intergranular quartz cement. Grains are yellow. The volume occupied by the cement and the intergranular pores together constitutes IGV. The IGV at deposition was even greater than the current IGV because compactional strain has figured into the porosity decline.
- C. Porous echinoderm grainstone with preserved intergranular pores (filled with a blue plastic resin). Note that compaction has caused local breakage of the cement (yellow arrows), leading to minor rearrangement of the primary porosity. Yellow oval indicates minor secondary grain dissolution porosity. Cretaceous, Mississippi, USA. Plane-polarized light image modified from Milliken and Choh (2011) (calcite is stained pink with alizarin red-S).
- D. Interpreted view of image C. The combined volume occupied by the intergranular pores c (darker blue) and the cement (blue mask) together constitutes IGV. The original porosity in this rock was at least as large as the IGV and perhaps greater. Grains are yellow.

Figure 2. Primary intragranular pores.

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4 A. Primary intragranular pores (filled with a blue plastic resin) within a gastropod
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6 fragment partially filled with detrital mud. Right side of gastropod contains a pore
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8 caused by a boring organism (red x); whether to classify this pore as “primary
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10 intragranular” versus “secondary bioerosion” is a technical debate that bears little on
11
12 the assigned character of the bulk porosity. Holocene sediment, Jamaica. Plane-
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14 polarized light image modified from Milliken and Choh (2011).
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19 B. Fusilinid foraminifer with chambers (former primary intragranular pores) filled by
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21 sparry calcite cement (red x). Permian, West Texas. Plane-polarized light image
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23 modified from Milliken and Choh (2011).
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26 Figure 3. Secondary pore types.
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29 A. Secondary intragranular pore filled with blue plastic resin. In addition to surviving
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31 remnants of the detrital feldspar, minor amounts of microporous kaolinite (Kr)
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33 replace the grain. Additional kaolinite cement (Kc) fills partially fills the intergranular
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35 pore space in the lower half of the image. Pennsylvanian, Kentucky. Plane-polarized
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37 light image.
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41 B. Interpreted view of image A. Surviving remnants of albitic feldspar are masked in
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43 pale purple.
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46 C. Intraclast/foraminifer grainstone with extensive secondary pore development.
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48 Permian, West Texas. Plane-polarized light image modified from Milliken and Choh
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50 (2011). Calcite is stained pink with alizarin red-S.
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53 D. Interpreted view of image C, based on a digital extraction of blue pixels (pores). Red
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55 outlines denote grains. Pores within the grain boundaries are secondary; pores
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57 external to the grains are primary intergranular pores. The IGV of this image is equal
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4 to the total image area minus the grain area. Most of the pores in this sample are not
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6 within the IGV.
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9 Figure 4. Grain replacement in which fabrics suggest a tight connection between mineral
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11 dissolution and precipitation that leaves little to no associated porosity. In such cases
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13 the replacement mineral typically displays euhedral terminations along the contact
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15 with the dissolving mineral that suggest a volume-for-volume replacement (Maliva
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17 and Siever, 1988).
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21 A. Fe-dolomite replacing detrital albite (ab) in a sandstone. Dolomite has nucleated
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23 on a detrital dolomite grain at breaks in the siderite overgrowth. Remnants
24
25 of the replaced feldspar are seen as gray inclusions scattered through the
26
27 Fe-dolomite. Back-scattered electron image.
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31 B. Euhedral pyrite (py) replacing a calcitic skeletal fragment in a calcareous
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33 mudstone. Back-scattered electron image.
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36 C. Fe-dolomite (purple) replacing Na-rich detrital feldspar (green) in an organic-rich
37
38 mudstone. Feldspar is also partially replaced by calcite (blue). X-ray map.
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41 D. Authigenic albite (ab) replacing carbonate allochems in a calcareous mudstone. X-
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43 ray map.
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46 Figure 5. Porosity inversion through diagenesis. The complex paragenesis in this sandstone
47
48 entails substantial dissolution of a portion of the unstable volcanogenic grains (yellow
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50 outlines). Cementation has primarily affected primary intergranular pores and includes an
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52 early generation of green chlorite cement (Cc) and a later generation of zeolite cement (Zc).
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54 Chlorite (Cr) and zeolite (Zr) have also precipitated as grain replacements within space
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56 opened by grain dissolution prior to cementation. Thus, grain dissolution has overlapped the
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4 timing of cement growth, a small portion of the grains dissolving prior to cementation but the
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6 greater bulk of dissolution post-dating cementation. A key point here is that the specimen is
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8 still recognizably sedimentary, with clear grain and intergrain components, despite the
9
10 massive alteration. Izu-Bonin Arc, western Pacific. Plane-polarized light image by Kathleen
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12 Marsaglia and modified from Milliken et al., 2007.
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16 Figure 6. Extreme diagenetic replacement that obscures the primary fabric. Pores in this sample
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18 cannot be readily placed into the context of the original depositional fabric. Yellow
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20 outlines are very tentative interpretations of the outer edges of former grains (possible
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22 ooids of originally calcitic or aragonitic composition) that have been replaced by euhedral
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24 to subhedral dolomite. Dolomite crystals within the interpreted grain volumes are
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26 classified as grain replacements and pores within those volumes are secondary. Dolomite
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28 outside of the interpreted grain volume is possibly cement and pores within that part of
29
30 the rock may be surviving intergranular pores. There is no discernible difference however
31
32 between the dolomite crystals within and without the interpreted grain volumes. In effect,
33
34 the sedimentary fabric of the rock is very nearly erased by the dolomitization and the
35
36 pores are best categorized as simply intercrystalline. Vacuoles that appear as brownish
37
38 microinclusions are intercrystalline pores. Further cementation would ultimately lead to a
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40 crystalline fabric that is essentially the same as those of metamorphic carbonate (marble).
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42 Permian dolomite, West Texas. Plane-polarized light image modified from Milliken and
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44 Choh (2011).
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53 Figure 7. Key technology that enabled the pore categorizations described in Figures 1-6. This
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55 method for enabling visualization of the pores is restricted to pores that are larger than
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4 the thickness of a thin section and to rocks with sufficient permeability to allow
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6 impregnation with the colored medium.
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9 Figure 8. Shale samples prepared for SEM.
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- 11 A. SE image of un-milled broken surface showing possible porosity or simply grain pluck-
12 outs indicated by black arrows. A large region of organic matter (OM) crosses the central
13 portion of the image.
14
15 B. BSE image of FIB milled surface on same sample as shown in A. Organic matter (OM) is
16 widely dispersed as stringers throughout the sample. Very little porosity is observed
17 (white arrows) suggesting that most of the apparent porosity visible in A is due to grain
18 pluck-outs.
19
20 C. BSE image of FIB milled surface displaying curtaining artifacts (near-vertical grooves
21 most strongly developed on right and left sides of image).
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23 D. BSE image of FIB milled surface showing calcite sputter redeposition (c) in organic
24 matter-hosted pores.
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41 Figure 9. Pore types in fine-grained sediment.
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- 43 A. Shallowly buried marine mud (Pleistocene) contains primary intergranular pores (red
44 arrows) as well as an abundance of primary intragranular pores within diatom fragments
45 (yellow arrow). Secondary electron image.
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50 B. Pores between K-phyllsilicate grains in a Cretaceous-age calcareous mudrock.
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4 C. A through-going transgranular fracture in a Mississippian phosphatic mudstone. The
5
6 former pore space is now filled with calcite (c) and quartz (q). The bright phase within
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8 the quartz is barite. Back-scattered electron image.
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11 D. Organic-matter hosted pores within organic which itself appears to be pore-filling.
12
13 Euhedral terminations on crystals (quartz) now surrounded by the organic matter required
14
15 open pore space at the time they were growing. Hence, paragenetic relationships suggest
16
17 that the organic matter is some type of residual hydrocarbon and the contained pores are
18
19 secondary and related to thermal maturation. Back-scattered electron image.
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24 Figure 10. OM-hosted pores within OM filling a secondary pore in a mudrock.
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- 26 A. In this combined secondary/back-scattered electron image, it is clear that the pores are
27
28 surrounded by organic matter. But little further interpretation can be obtained. Is the
29
30 organic matter detrital or diagenetic? Are the pores primary or secondary?
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33 B. X-ray map of the same field of view seen in A. Magnification is somewhat beyond the
34
35 ideal for this method as indicated by the fuzzy borders on the various regions mapped for
36
37 individual elements. The fuzziness arises because the interaction volumes for X-ray
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39 generation are larger than some of the features being imaged. Yellow maps K-
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41 phyllosilicates, dark blue maps calcite, red maps quartz, aqua maps Na-feldspar. The
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43 dashed dark blue line marks the outer edge of a detrital feldspar grain. The dotted pale
44
45 blue line denotes a former secondary pore within the feldspar. Because the organic matter
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47 fills a secondary pore it is interpreted as a residual hydrocarbon (RH) phase). The pores
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49 within the feldspar are clearly secondary, but it remain uncertain whether these pores are
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51 simply residual, un-filled feldspar dissolution pores or pores that arose from thermal
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53 decomposition of the residual hydrocarbon.
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Figure 11. Cements in larger primary intragranular pores in mudrocks.

- A. Pyrite crystals filling an intact coccosphere in a calcareous ooze. Pleistocene, eastern Mediterranean. Back-scattered electron image of an Ar-ion milled surface.
- B. Dark-luminescing sparry calcite cement (cc) filling spaces within bright-luminescing calcified radiolaria and other allochems. Careful inspection reveals the same dark-luminescing material also fills spaces between the clay-size carbonate particles that compose most of the sediment. Cold-cathode cathodoluminescence image. Mississippian, Barnett Shale.

Table

Table 1. Imaging methods applied to sedimentary rocks.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

mechanical damage during grinding plucks material that reveals the underlying clear adhesive and glass.

Figure 8

Figure 9

Figure 10

Figure 11

Table 1

Table 1. Methodologies for imaging sedimentary rocks.

Method	Practical Resolution	Compositional information	Sample preparation	Conductive Coating [#]	Special considerations: Sample prep	Special considerations: Other	Use in Sedimentary Petrology	
Light Microscopy								
Reflected light methods								
1	Stereo reflected light	10 μm	by skilled interpretation	broken surfaces, thin sections, polished sections	none	generally < 100x instrument magnification	low-magnification view of surface texture; component size, shape, and color	
2	Reflected, polarized light ¹	1 μm	yes	polished sections or surfaces	usually none, C-coating OK		mineralogy, crystal size, shape, luster, and color of components that do not transmit light	
Transmitted light methods								
3	Transmitted, plane-polarized light (ppl) ²	1 μm	yes	thin sections or polished sections; 30 μm thickness standard; thinner if the rock does not transmit light well	usually none, C-coating OK	imaging of pores requires use of colored impregnation media	mineralogy; crystal and pore size and shape in materials that transmit light	
4	Transmitted, cross-polarized light (xpl) ²	1 μm	yes	thin sections or polished sections; 30 μm thickness standard; thinner if the rock does not transmit light well	usually none, C-coating OK	slight un-crossing of polarizers yields better photography	mineralogy; crystal size and shape in materials that polarize light	
5	Confocal transmitted light ³	0.5 μm	by skilled interpretation	thick sections; up to 500 μm data depth	none	requires translucent specimen	component size and shape in 3D; used mostly for pore imaging and characterization of microbial precipitates	
6	Real-time 3D transmitted light microscopy ⁴	200 nm	by skilled interpretation	polished sections; up to 100 μm thick	usually none, C-coating OK	requires translucent specimens	component size and shape in 3D	
Stimulated emissions								
7	UV-fluorescence ⁵	1 μm	by skilled interpretation	polished sections or surfaces	none	UV fluorescent dye can be used to highlight microporosity	trace element zoning, organic matter maturity; microbe detection; micropore distribution	
8	Cold-cathode cathodoluminescence ⁶	1 μm	by skilled interpretation	polished sections or surfaces	none		trace element variations within mineral species	
9	Coherent anti-Stokes Raman Scattering (CARS) ⁷	1 μm	contrasts chemical compounds through a sensitivity to bonding	polished surface	no	very new to geosciences	organic matter composition	
Scanning Electron Microscopy*								
10	Secondary electron (SE) imaging ⁸	1 nm	no	broken, polished, or ion milled surfaces	numerous possible coatings	samples need to generally clean and dry, coating may be omitted in low vacuum imaging at cost of resolution	SE contrast can be difficult to interpret. SE more susceptible to charging.	component shapes, sizes
11	3D SE imaging ⁹	1 nm	no	progressive slices imaged after milling by focused ion beam (FIB)	any coating will be removed by FIB	carbonate samples present redeposition issue for FIB	image volume limited to a few microns across	component shapes, sizes in 3D
12	Back-scattered electron (BSE) imaging ¹⁰	5 nm	by skilled interpretation in combination with EDS elemental identification	polished or ion milled surfaces	carbon or thin metallic	carbonate samples present redeposition issue for ion milling	distinction between materials not as good with high atomic number materials	compositional information; component shapes, sizes
13	Energy-dispersive spectroscopy (EDS) X-ray mapping ¹¹	0.5 μm	yes, for major, some minor elements, Boron and heavier elements	polished or ion milled surfaces	carbon or thin metallic	quantitative EDS requires very flat, homogeneous surfaces, conductive coating must be of known thickness	beam energies sufficient to cause damage to some materials	mineral shapes, sizes

14	Wave-length dispersive spectroscopy (WDS) X-ray mapping ¹¹	0.5 µm	yes, for major, minor and trace elements; Na and heavier elements	polished or ion milled surfaces	carbon		beam energies sufficient to cause damage to some materials	mineral shapes, sizes; compositional variations within mineral species
15	Cathodoluminescence (CL) imaging ⁶	0.5 µm	by skilled interpretation	polished or ion milled surfaces	carbon/none		beam energies sufficient to cause damage to some materials; imaging area limited to >150 X machine magnification; lower magnification images require mosaic mapping	compositional information; component shapes, sizes
16	Charge-contrast (CC) imaging ¹²	10 nm	by skilled interpretation	polished surfaces	none		requires low-vacuum operation	component shapes, sizes; compositional variation within mineral species, defects
17	electron back-scatter diffraction (EBSD); orientation contrast imaging ¹³	10 nm	mineralogy	polished or ion milled surfaces	carbon	samples need to be especially clean and flat	clays problematic	mineralogy; crystal size, shape, and orientation

Transmission Electron Microscopy

18	TEM imaging ¹⁴	.1 - .2 nm	Bright field for mass-thickness contrast, dark field for crystallographic contrast; minerals can be identified by skilled interpretation	thinned specimens (<100 nm)	none	want to reduce amorphous layer from milling, samples can be fragile	stringent room requirements	component size, shape
19	Selected area electron diffraction (SAED) ¹⁵	.1 - .2 nm	yes	thinned specimens (<100 nm)	none	sample should be thin enough that 2 grains are not overlying each other	all materials within the diffraction aperture will contribute to pattern	mineralogy, crystal structure
20	Electron Energy Loss Spectroscopy (EELS) ¹⁶	.1 - .2 nm	yes	thinned specimens (<100 nm)	none		Typically must consult library of spectra for identification, beam damage an issue	elemental composition, phase

Scanning Transmission Electron Microscopy

21	bright-field (BF) ¹⁷	.1 - .2 nm	mass-thickness contrast; minerals can be identified by skilled interpretation	thinned specimens (<100 nm)	none	same as TEM	can be performed in a properly equipped SEM or a TEM	component size, shape, higher resolution EDS
	annular dark field(ADF) ¹⁸	.1 - .2 nm	crystallographic contrast; minerals can be identified by skilled interpretation	thinned specimens (<100 nm)	none	same as TEM	can be performed in a properly equipped SEM or a TEM	component size, shape, crystallinity
22	high-angle annular dark field (HAADF) ¹⁹	.1 - .2 nm	atomic number contrast; minerals can be identified by skilled interpretation	thinned specimens (<100 nm)	none	same as TEM	can be performed in a properly equipped SEM or a TEM	component size, shape

23	Helium Ion Microscopy ²⁰	< 1 nm	atomic number contrast from backscattered ions	broken, polished, or ion milled sections	no		charge control by flood gun may be needed	component size, shape
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Secondary Ion Mass Spectroscopy

24	SIMS imaging ²¹	2-3 Å	major, minor, trace, and isotopic compositions	polished surfaces	no		Ion implantation/damage can be an issue; charge control by flood gun	trace element and isotopic variations within mineral species
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25		FIB-SIMS ²²	20 nm	major, minor, trace, and isotopic compositions	polished surfaces	no		Ion implantation/damage can be an issue; charge control by flood gun	trace element and isotopic variations within mineral species
Atomic Force Microscopy									
26		AFM imaging ²³	Vertical: 1-2 Å; Horizontal: 1-2 nm; Field of view limited to ~100 µm.	Limited compositional information by interpretation	Sample must be relatively flat	no		Large topographical features can damage tip. Tip convolutions result in inaccurate representation of topography.	component size and shape
27		Peak-force QNM ^{TM24}	< 5 nm	Limited compositional information by interpretation	Sample must be relatively flat	no		Large topographical features should be avoided due to tip damage	mapping of elastic moduli in specific components; possible use in discriminating OM types
28	X-ray Computed Tomography (XCT) ²⁵		1 µm for microXCT; 50 nm for nanoXCT; Higher magnifications require thinner samples or longer exposure times	composition differences based on density and atomic number	Samples usually shaped into cubes or cylinders of mm dimensions	no	nanoXCT requires small sizes	Contrast agents can be added to highlight accessible porosity. For nanoCT, laser ablation or FIB milling used to create optimal sample size.	component size, shape in 3D; including fluid distributions
29	Scanning Acoustic Microscopy ²⁶		1 µm	Limited compositional information by skilled interpretation	polished surface	no			Topography and acoustic impedance (elastic properties) of constituent materials
30	Small-angle X-ray Scattering (SAXS) ²⁷		1 nm	none	sample dimension considerations of apparatus (mm to cm)	no			component size and shape
31	Small-angle Neutron Scattering (SANS) ²⁸		1 nm	determination of pore host material	sample dimension considerations of apparatus (mm to cm)	no	deuterated fluids better for saturation experiments due to higher scattering length density	More sensitive to light elements than SAX; limited to features < 100 nm	component size and shape
32	Synchrotron X-ray Fluorescence Imaging (SXRF) ²⁹		1 µm	major, minor, and trace elements	roughly flat or polished surfaces	no			small-scale elemental mapping

SEM imaging performed without a coating requires an instrument capable of operation at low vacuum.

* SEM resolutions are reported for techniques performed on a field-emission instrument

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