

Impact of Pore Connectivity on Quantification of Mineral Accessibility in Sandstone Samples

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Abstract

Characterization of microscale features and mineral distributions in rock samples can be facilitated non-destructively with imaging analysis. Scanning electron microscopy (SEM) with backscatter electron (BSE) and energy dispersive spectroscopy (EDS) is particularly valuable and can be utilized to identify minerals. Mineral segmentation coupled with quantitative image processing can yield mineral volume fractions and accessibility from these images. Prior estimates of mineral accessibility from images have improved simulations of mineral reaction rates but it is unclear how pore connectivity should be accounted for. This is further complex in samples with clay minerals where nanopores in clays need to be considered. Here, impacts of different approaches to assess pore connectivity on quantification of mineral accessibility are considered for seven sandstone samples with varying composition. Mineral accessibilities are calculated by counting

interfacial pixels between associated minerals and adjacent pores from the 2D mineral segmented maps. Three types of accessibility are considered: the first approach accounts for all the macropore space, the second approach considers only the 2D connected macropores, and the third approach includes 2D connected porosity considering nanopores in clays. Observed variations in accessibility for most mineral phases are within one order of magnitude when nanopore connectivity is considered and thus not anticipated to largely impact the simulated reactivity of samples. However, greater variations were observed for clay minerals which may impact long-term simulations (years). Larger variations in accessibility were also noted for carbonate minerals but only some samples contained carbonate phases and additional data is needed to assess the trends.

Keywords: Mineral Accessibility, Mineral Segmentation, Nanopore connectivity, Scanning Electron Microscopy, Effective Porosity

1. Introduction

Understanding mineral reactions and reaction rates in porous media are critical to assessing and predicting transport in reactive environmental systems, including natural weathering processes¹⁻³, contaminant transport⁴⁻⁸, CO₂ injection for storage^{9,10} or enhanced oil recovery¹¹⁻¹⁴, and compressed energy storage^{15,16}. In these and other systems, mineral dissolution occurs due to perturbations from equilibrium.

Mineral dissolution rates are typically determined using batch experiments with single mineral phases, but there is a noted discrepancy in the rate of reaction observed in the laboratory in comparison with field observed reaction rates^{2,17-20}. In part, this is due to porous media effects and a misestimation of mineral reactive surface area in porous media²¹⁻²³. Advanced imaging of

natural porous media has revealed that mineral surfaces may be occluded by clay mineral coatings or limited by pore connectivity such that those surfaces are not accessible for reaction ^{22,24–26}. Mineral accessible surface areas, those that will be in contact with reactive fluids, have been noted to improve simulation of mineral reaction rates in multi-mineralic porous media as compared to other more traditional means of reactive surface area estimation ²². Combining surface roughness scaling factors can even improve the accessible surface area estimation to the atomic level ²⁷. As such, mineral accessibility may better reflect the proportion of mineral phases available for reaction in porous media as compared to mineral volume or weight fractions.

Mineral accessibilities can be quantified using imaging analysis ^{24,26}. Mineral maps can be created by processing 2D Scanning Electron Microscopy (SEM) images where individual mineral phases are identified by combining backscattered electron (BSE) and energy-dispersive x-ray spectroscopy (EDS) images ^{22,24,26}. Properties of the sample including porosity, mineral volume fractions (abundances), and mineral accessibilities are then determined from the mineral map by pixel counting ^{22,25,26}.

Mineral accessibility is quantified by computing the number of mineral pixels of each phase at the pore-mineral interface. In the simplest approximation, this assumes reactive fluids may be present in all pore spaces. However, pore connectivity may limit fluid flow and result in some regions that are inaccessible to fluid flow. This has been accounted for by evaluating pore connectivity using a burning algorithm to map connected pores in the 2D mineral map and deeming only those minerals adjacent to the identified connected pore pixels as accessible ^{22,26}. 2D SEM imaging cannot capture nanopore connectivity, but high-resolution Focused Ion Beam SEM (FIB-SEM) imaging of clay minerals has revealed clay minerals have abundant, well-connected nano porosity ^{22,26}. As such, nanopores in clays may not limit but instead, contribute to overall pore

connectivity and alter the relative proportion of mineral's availability^{22,26}. However, this approach still only reflects connectivity in 2D such that assuming all pores are connected may better reflect actual pore connectivity of sandstone samples. While pore connectivity can be readily determined in 3D from 3D X-ray computed tomography (X-ray CT) images, mineral phases, and thus mineral accessibility, cannot. Additional resolution limitations may underestimate overall 3D connectivity estimates. As such, mineral accessibilities can only be quantified in 2D images, but it is unknown to what extent estimated mineral accessibility would change given variations in estimated pore connectivity.

The objective of this work is to enhance understanding of mineral accessibility in sandstone samples and variations in image quantified mineral accessibilities due to different pore connectivity approaches. Here, the impact of accounting for pore connectivity on mineral accessibility is considered for seven sandstone samples of varying compositions. Pore connectivity and mineral accessibility are determined, excluding, and including nanopore connectivity, and results compared to discern the impact of pore connectivity estimates on the quantification of mineral accessibility.

2. Materials and Methods

2.1 Samples

Seven sandstone samples with varying clay content were selected for analysis in this work. This includes samples from the Bandera Grey, Bandera Brown, Bentheimer, Kentucky, and Torrey Buff formations obtained from Kocurek Industries. Two additional samples from the Lower Tuscaloosa and Paluxy formations were obtained from the Geological Survey of Alabama. From X-ray Diffraction (XRD) analysis provided by Kocurek Industries and prior evaluation of similar

86 samples in the literature ^{28,29}, these samples are predominantly quartz (59%-94%) with additional
87 feldspar, carbonate, and clay minerals (Table 1).

88 **Table 1:** Mineral abundances (wt%) from XRD analysis as obtained from Kocurek Industries¹,
89 Soong et al. (2016)² and Guan (2012)³

Sample\Mineral	Quartz	Albite	K- Feldspar	Calcite	Dolomite	Kaolinite	Illite	Chlorite	Smectite	Siderite
Bandera Grey ¹	59	12	0	0	15	3	10	1	0	0
Bandera Brown ¹	66	13	2	3	0	7	11	2	0	0
Bentheimer ¹	94.4	1.2	1.2	0.5	0	0	0	0	0	0
Kentucky ¹	66	17	3	0	0	trace	14	0	0	0
Torrey Buff ¹	48	0	6	0	24	16	7	0	0	0
Lower Tuscaloosa ²	92	0	3	0	1	1	1	2	0	0
Paluxy ³	66	1	3	0	0	13	7	1	0	6

90 Polished thick sections (0.5 cm thickness) (Kocurek Industries samples) and polished thin
91 sections (Geological Survey of Alabama samples) were created by Applied Petrographic Services,
92 Inc. (Westmoreland, Pennsylvania) for SEM imaging analysis. To prepare for SEM imaging, a
93 conductive carbon coating was applied to each thin section using EMS 550× Sputter Coating
94 Device at Auburn University. Thick sections were left uncoated.

95 2.2 Image acquisition and mineral properties quantification

96 Mineral properties including porosity, mineral abundance, and mineral accessibility were
97 quantified from 2D SEM BSE and EDS images. SEM BSE images of the seven samples were
98 captured using a ZEISS EVO 50VP Scanning Electron Microscope at Auburn University. Carbon–
99 coated thin sections were imaged under high vacuum mode while the uncoated thick sections were

100 imaged under variable pressure mode. The resolution and size of each image are given in
101 supplementary information (Table S1). A representative elementary volume (REV) analysis was
102 carried out on collected images for each sample to ensure each image area was sufficient. SEM
103 BSE images were first manually thresholded in ImageJ to separate grain and pore pixels. Several
104 sub-areas of increasing size were selected from the segmented image and the porosity was
105 computed by pixel counting.

106 EDS elemental maps were also obtained for each sample to help identify mineral phases. Images
107 were registered in ImageJ and additional processing and mineral segmentation of the images
108 followed the approach used in Landrot et al. (2012) and Beckingham et al. (2016)^{26,30}. Briefly,
109 SEM-EDS elemental maps were enhanced with filters in ImageJ and customized noise reduction
110 Matlab codes. Minerals were then identified based on elemental maps and SEM BSE grayscale
111 intensity. Each pixel was assigned to a specific mineral and expressed as a unique color, creating
112 a processed mineral map. This part of the processing was performed in Matlab (original code
113 modified for each image) and ImageJ.

114 Following image segmentation, mineral abundances were calculated by counting mineral pixels
115 with the same color while mineral accessibilities were calculated by counting mineral pixels
116 adjacent to pore pixels. Mineral abundance refers to the volume fraction of each mineral phase,
117 and mineral accessibility refers to the percentage of each mineral's surface that is adjacent to the
118 pores. To determine accessibilities, pore-mineral interfacial pixels were first identified using codes
119 written in Matlab. The accessibility of each mineral phase was then calculated from the number of
120 interfacial pixels of each mineral phase divided by the total number of interfacial pixels.

121 Here, three different means of calculating mineral accessibility were considered. This included
122 defining interfacial pixels as mineral pixels adjacent to 1) pores identified in the processed mineral

map, which will be referred to as macropores, 2) connected macropores identified in the processed mineral map, and 3) connected nano and macropores in processed mineral maps. In cases that considered connected pores, these pore pixels were identified by using a burning algorithm after Landrot et al. (2012)²⁶. The algorithm first identifies pore pixels at the image edges then searches inward for adjacent (connected) pore pixels, continuing inwards until it completes searching in all four directions²⁶. Identified connected macropores are displayed in white and connected nanopores in clays presented in three different colors for the three different clays. Connected porosity was calculated as the total number of connected pore pixels divided by the total pixels of the image. In the third estimation, we assume all clay minerals have abundant, well-connected nanoporosity as observed in prior Focused Ion Beam (FIB) SEM imaging analysis of clay minerals^{26,30}.

3 Results

3.1 Image processing and mineral property quantification

SEM BSE images, mineral phase segmented maps, and 2D pore connectivity images were produced for each sample. Mineral abundance obtained from the 2D segmented map is presented in Table 2. As expected from the prior mineral abundance data, quartz, feldspars, carbonates, and clay, as well as some additional minerals like siderite, zircon, mica (muscovite and biotite), and some oxides (ilmenite, anatase, and magnetite) were identified in the samples.

Table 2: Mineral abundances (vol%) and accessibilities (%) determined from the 2D mineral segmented maps using three approaches.

Sample	Minerals	Abundance (vol%)	Accessibility (All Macro Pores)	Accessibility (Only Connected Macro Pores)	Accessibility (Connected Macro & Nano Pores)
Bandera Grey	Quartz	63.46	57.98	70.82	62.63

	K-feldspar	12.12	7.32	6.12	5.53
	Albite	10.22	8.81	7.28	7.45
	Calcite	5.69	1.15	1	0.84
	Illite	6.39	23.34	14.78	23.45
	muscovite	0.68	0.45	0	0
	Titanium Oxide	0.28	0.23	0	0.09
	Biotite	1.14	0.7	0	0
Bandera Brown	Quartz	73.48	62.58	69.42	54.81
	K-feldspar	8.33	5.47	2.57	5.48
	Albite	10.24	5.57	4.2	6.02
	Calcite	0.007	0.01	0	0
	Kaolinite	4.31	16.05	12.86	21.83
	Illite	1.17	4.31	2.7	6.35
	Chlorite	0.48	2.33	4.5	3.45
	Titanium Oxide	0.47	0.14	0.11	0.08
	Iron Oxide	1.49	3.53	3.63	1.97
Bentheimer	Quartz	95.32	83.65	84.79	80.05
	K-feldspar	2.71	2.72	2.35	2.99
	Calcite	0.0003	0	0	0
	Kaolinite	1.64	13.24	12.6	16.71
	Ilmenite	0.4	0.39	0.25	0.24
Kentucky	Quartz	62.58	47.49	33.25	34.29
	K-feldspar	2.95	2.2	0.27	4.97
	Albite	16.79	10.67	14.05	10.37
	Zircon	0.37	0.06	0	0.34
	Ilmenite	0.29	0.11	0.5	0.99
	Illite	11.73	35.51	49.68	31.25
	Muscovite	2.55	2.51	0.37	4.79
	Titanium Oxide	0.17	0.1	0.05	0.71
	Iron Oxide	2.6	1.35	1.83	12.27
Torrey Buff	Quartz	56.73	53.38	57.74	51.68
	K-feldspar	5.83	2.87	1.82	3.74
	Iron-rich dolomite	12.04	2.78	1.53	1.65
	Dolomite	13.28	3.71	1.38	1
	Kaolinite	10.62	34.36	35.04	39.25
	Illite	0.59	2.62	2.17	2.62
	Zircon	0.19	0.015	0.006	0.003
	Titanium Oxide	0.34	0.05	0.11	0.05
	Iron Oxide	0.37	0.22	0.18	0
Lower Tuscaloosa	Quartz	92.03	79.32	83.33	79.48
	K-feldspar	1.58	3.32	1.47	2.4
	Albite	0.49	0.58	0.39	0.3

	Dolomite	1.48	1.67	1.17	2.13
	Kaolinite	3.67	14.82	13.41	15.51
	Muscovite	0.53	0.28	0.22	0.18
Paluxy	Quartz	69.31	51.35	51.96	47.24
	K-feldspar	1.21	1.56	1.04	1.05
	Albite	24.5	25.86	20.02	17.86
	Calcite	0.78	0.46	0.14	0.96
	Kaolinite	2.26	16.9	24.35	28.12
	Illite	0.24	2.04	1.38	3.24
	Siderite	0.29	0.48	0.37	0.35
	Titanium Oxide	0.81	0.39	0.14	0.24
	Muscovite	0.6	0.97	0.6	0.95

As discussed in section 2.2, mineral accessibilities were quantified for every mineral in each sample. The accessibility data is presented in Table 2. These values indicate the proportion of each mineral at the pore-grain interface. It is of interest to consider the interfaces of the grains that will be in contact with the potential reactive fluid. If the pore space is well connected, reactive fluid may be in all identified pores. However, limitations in pore connectivity can occur and restrict which mineral surfaces are accessible to the reactive fluid. Both scenarios are considered here in calculations of mineral accessibility. Pore connectivity is identified using a burning algorithm where connected porosity is first identified only considering macropores and then considering connectivity through clay nanopores. Connected macropores are shown in white in Figures 1-7 (d), while three different colors are used to present the nanopore connectivity in clays in Figures 1-7 (e): kaolinite in turquoise, chlorite in cyan, and illite in teal.

3.1.1 Bandera Grey

The SEM BSE and mineral phase segmented map of the Bandera Grey sandstone sample is shown in Figure 1 (a and b). It is predominately comprised of quartz and two feldspar minerals, K-feldspar and albite. The calculated porosity from the BSE image is 15%. Accessibility is calculated for all the minerals considering the three approaches. Figure 1c shows the mineral

segmented map where all the macropores are assumed to be filled with reactive fluid and represented in white color. Similar to the highest abundance, quartz has the highest accessibility. The accessibility of the clay phase, smectite/illite is four times higher than the abundance of clay minerals.

When considering macropore connectivity, the sample has very low pore connectivity, which is reflected in Figure 1d. The corresponding effective porosity is 1.66%. Considering connected macropores, quartz has the highest accessibility among all the mineral phases, followed by smectite/illite. The accessibility of K-feldspar and albite reduce when considering connected macropores to 6.12% and 7.28%, respectively. Mica minerals, muscovite and biotite, are not accessible due to low macropore connectivity. Accounting for multi-scale pore connectivity, including nanopore connectivity through smectite/illite, there is a minor increase in the effective porosity (from 1.66% to 2.21%). Quartz accessibility is the highest and agrees well with quartz abundance, whereas K-feldspar and albite have accessibilities approximately half of their abundances. Accessibility values increase significantly for smectite/illite in comparison with only considering macropore connectivity.

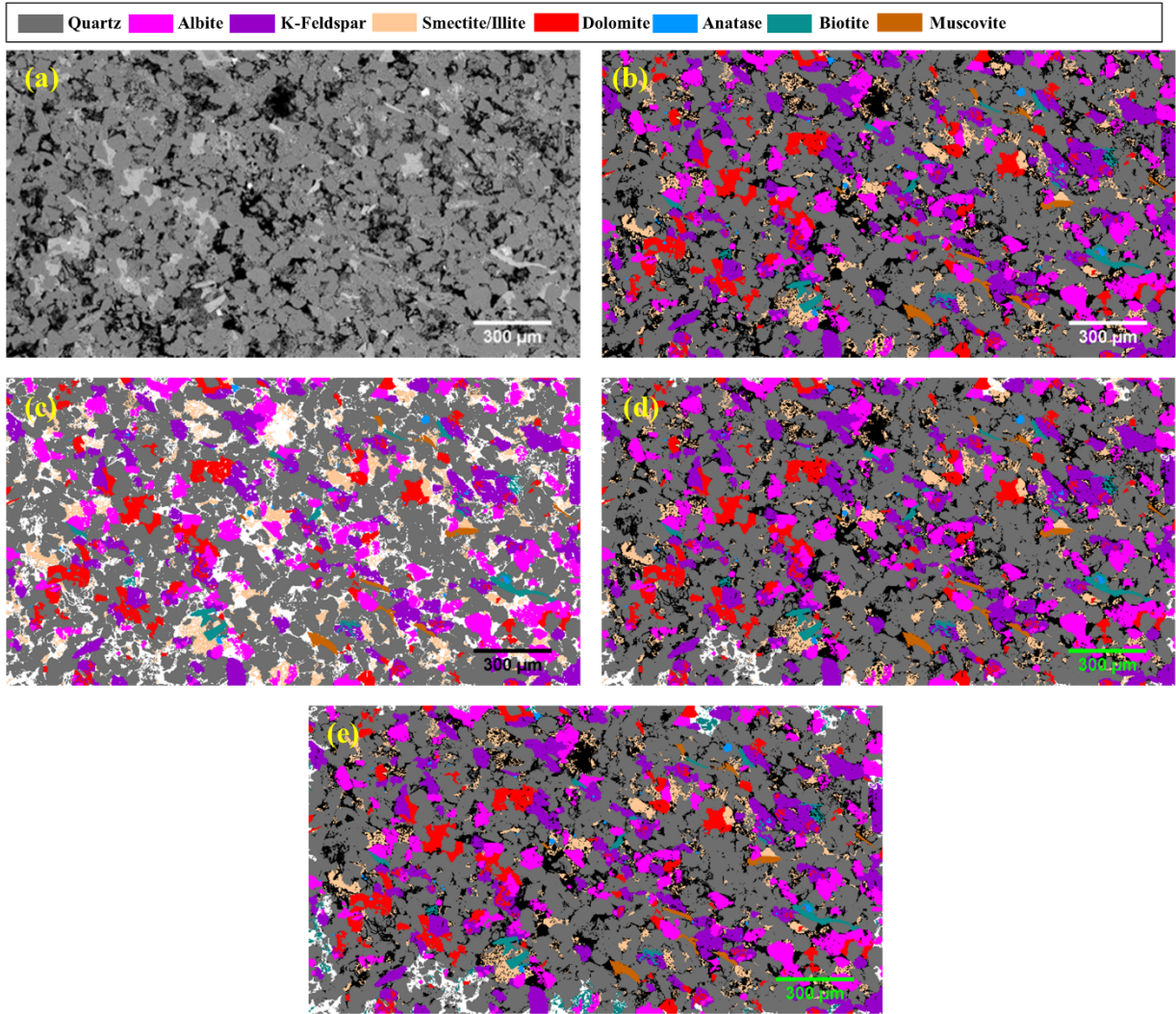


Figure 1: a) SEM BSE image of sample collected from Bandera Grey formation; b) mineral phase segmented map; c) mineral map considering all macro pores accessible; d) mineral map considering macro pore connectivity; e) mineral map including nano pore connectivity

3.1.2 Bandera Brown:

The SEM BSE image of the Bandera Brown sample and corresponding processed mineral map are in Figures 2 (a and b). A total of nine minerals are identified, with the majority of the sample comprised of quartz. There are three clay minerals – kaolinite, illite, and chlorite with a

total abundance of 5.96%. The porosity is calculated to be 21%. When all the macropores are considered, the accessibility of quartz is slightly less than the abundance while accessibilities are significantly less than abundances for K-feldspar and albite. On the other hand, the accessibility of clay minerals is about four times their abundance. Calcite accessibility is similar to its abundance.

Consideration of macropore pore connectivity significantly reduces the effective porosity to 5.2%. The accessibility of quartz remains high and close to its abundance. While K-feldspar and albite have higher abundances than clay minerals (kaolinite, illite, and chlorite) the accessibility of the clay minerals is higher. Calcite only has 0.007% abundance, and it is embedded in quartz grains, therefore, its accessibility is 0%. Figure 2e shows the mineral map considering nanopore connectivity in all three clays in the sample. Accounting for nanopore connectivity increases the effective porosity to 8.91%. Also, more albite and K-feldspar become accessible (see red boxes in Figure 2e). The accessibility of kaolinite also increases significantly from 12.86% to 21.83%.

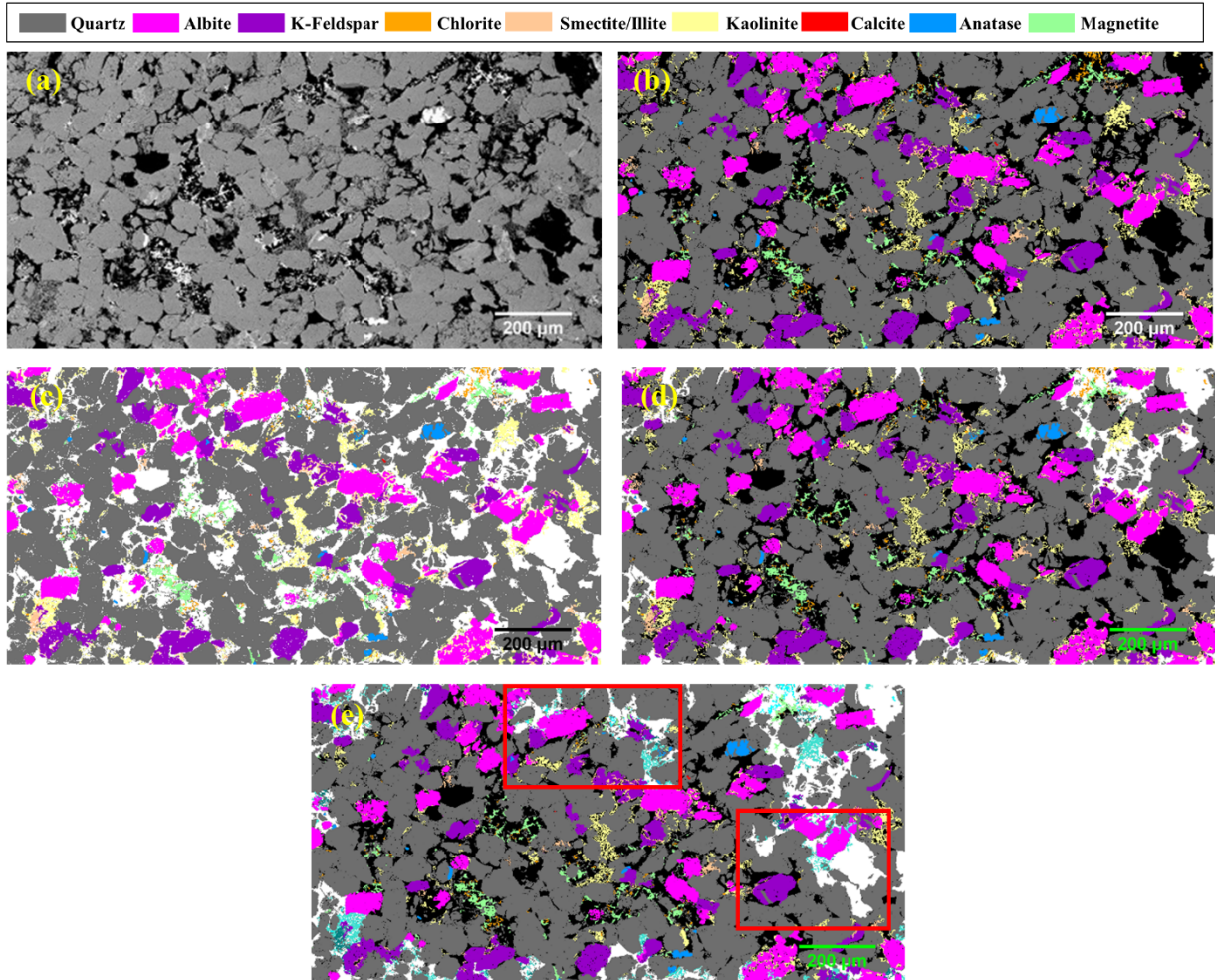


Figure 2: a) SEM BSE image of the sample collected from Bandera Brown formation; b) mineral phase segmented map c) mineral map considering all macropores accessible; d) mineral map considering macropore connectivity; e) mineral map including nanopore connectivity.

3.1.3 Bentheimer:

There are six mineral species identified in the BSE image of Bentheimer sample (Figure 3). Quartz has more than 95% abundance. This sample has a high porosity, 34.92%, measured from the 2D mineral map. When considering all macropores as accessible (Figure 3c), quartz has an accessibility of 83.65%, which is less than the abundance of quartz. The accessibility of K-feldspar

204 agrees well with its abundance, whereas calcite is inaccessible. The accessibility of kaolinite is
205 13.24%, significantly higher than its abundance.

206 Considering mineral interfaces accessible to connected macropores (Figure 3d), 84.79% are
207 quartz, which is similar to when connectivity was not considered. About 12.6% of accessible
208 surfaces are kaolinite, which is significantly higher than the relative abundance of kaolinite.
209 Accounting nanopore connectivity (Figure 3e) decreases accessibility of quartz and increases
210 accessibility of k-feldspar and kaolinite. Calcite is inaccessible in this case too. Effective porosities
211 reduced to 15.68% and 18.45% considering connectivity in macro and nanoscales respectively.

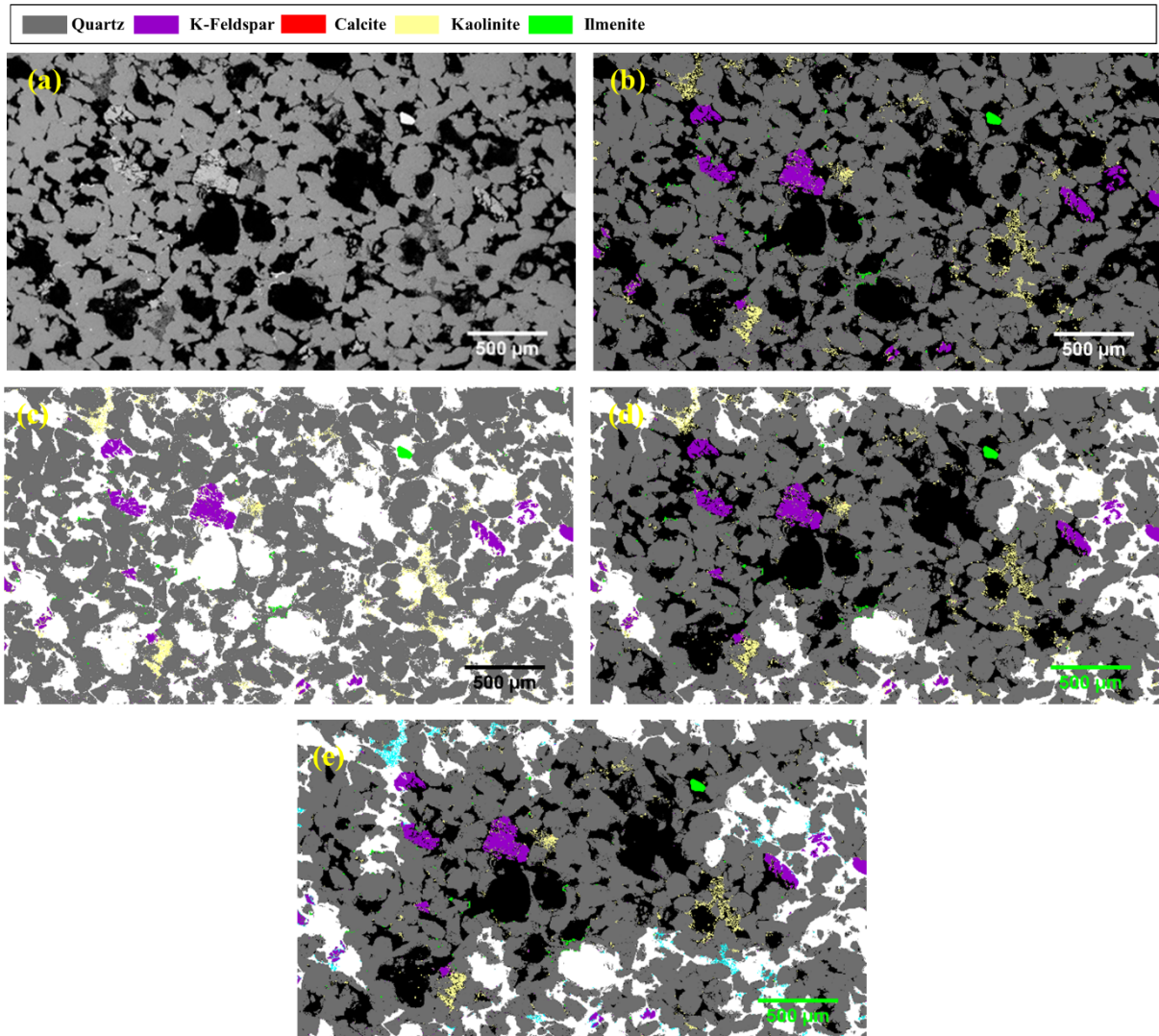


Figure 3: a) SEM BSE image of Bentheimer sandstone; b) mineral phase segmented map c) mineral map considering all macro pore accessible; d) mineral map considering macro pore connectivity; e) mineral map including nano pore connectivity

3.1.4 Kentucky:

The original and processed images for the Kentucky sandstone sample are shown in Figures 4 (a and b). Among the seven samples considered in this work, the Kentucky sandstone sample has the lowest porosity. The porosity calculated from the BSE image (Figure 4a) is 13.25%. Nine

220 mineral species are identified in the image and mapped in Figure 4b. Quartz is the most dominant
221 phase with over 62% abundance, followed by albite and smectite/illite. Figure 4c shows the
222 mineral segmented map when all the mineral surfaces are considered accessible. Quartz, which is
223 the dominant phase, has an accessibility of 47.49%, which is significantly lower than its
224 abundance. The accessibility of K-feldspar and muscovite agree well with their abundances while
225 illite accessibility is more than three times its volume fraction.

226 Having the lowest porosity, the sample is also very low on pore connectivity when only
227 macropores are considered (effective porosity 1.25%). As for accessibility, smectite/illite has the
228 highest accessibility, 49.68%, which is significantly higher than its abundance and its accessibility
229 when connectivity is not considered. The accessibilities of quartz and albite are 33.25% and
230 14.05%, respectively, which is less than the abundance of quartz but similar to the abundance of
231 albite. Zircon is not accessible to the connected pore space. Consideration of nanopore connectivity
232 allows a lot of magnetite grains to be accessible (red boxes, Figure 4e) resulting in an increase in
233 accessibility of 12.27% from 1.83%, while for albite and illite, the values decrease. The effective
234 porosity increases to 4.27% when nanopore connectivity is included.

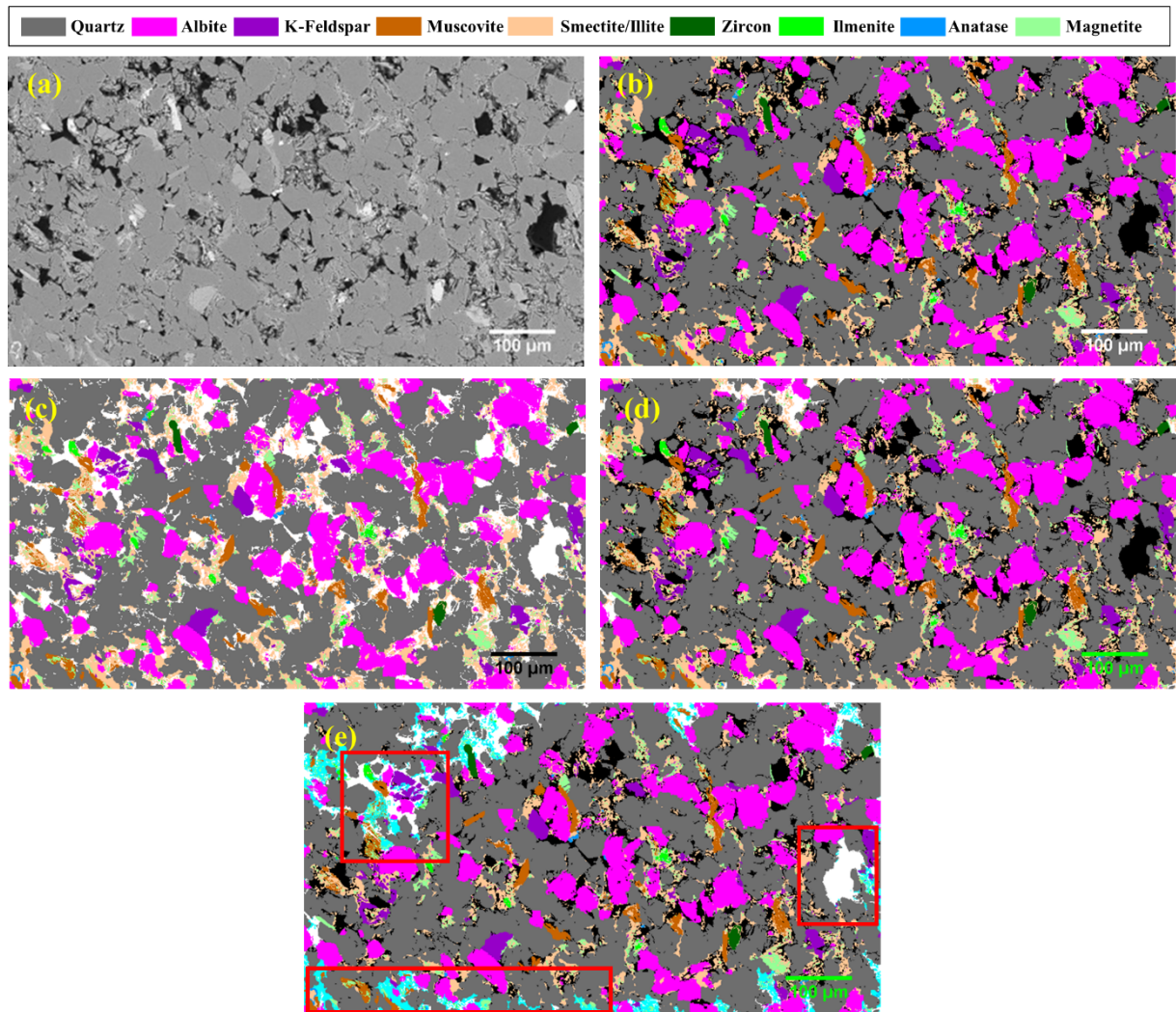


Figure 4: a) SEM BSE image of Kentucky sandstone; b) mineral phase segmented map; c) mineral map considering all macropore accessible; d) mineral map considering macropore connectivity; e) mineral map including nanopore connectivity

3.1.5 Torrey Buff

Figures 5 (a and b) show the original BSE SEM image and Torrey Buff sample's colored mineral segmented map, respectively. There are eight different minerals identified, and more than half of the total volume is comprised of quartz. Another major phase identified from the mineral map is dolomite, half of which is rich in iron. The sample has a high amount of clay. The calculated

porosity from the mineral segmented map is 20.3%. When accessibility is calculated considering all the macropores, quartz has a similar value for accessibility as abundance. K-feldspar and dolomite have accessibilities significantly lower than their abundance. Both of the clay minerals have high accessibility (34.36% and 2.62%) as compared to abundance.

When considering connected macropores, quartz has the highest accessibility, similar to its abundance, while kaolinite has significantly higher accessibility than abundance. As the sample has a higher amount of clay distributed throughout the sample (Figure 5b) considering nanopore connectivity (Figure 5e) significantly increases the effective porosity from 3.22% to 10.88%. The resulting accessibility of quartz decreases, while for K-feldspar, kaolinite, and illite, the values increase. The effective porosity also increases from 3.22% to 10.88% when nanopore connectivity is included.

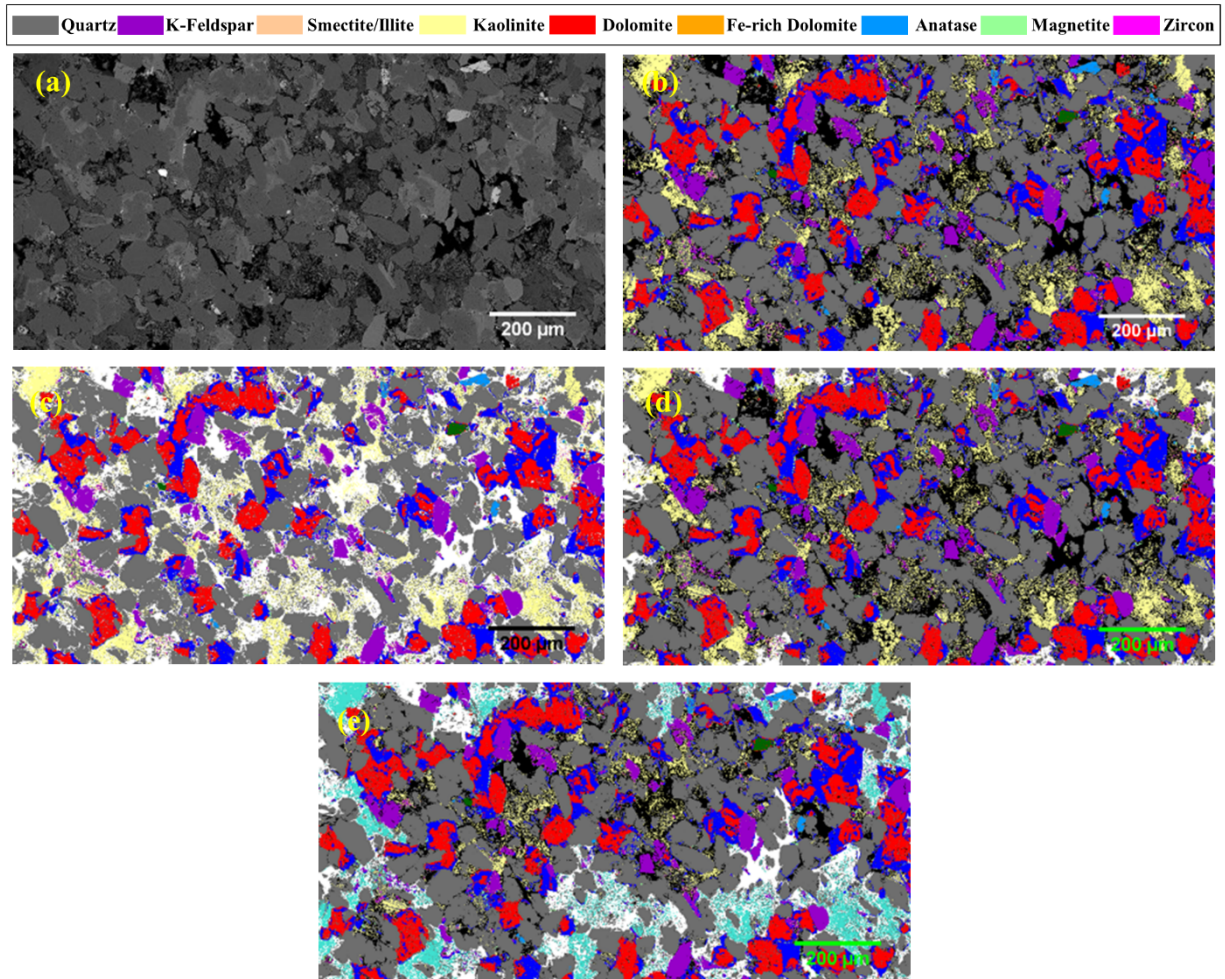


Figure 5: a) SEM BSE image of sample collected from Torrey Buff formation; b) mineral phase segmented map; c) mineral map considering all macropores accessible; d) mineral map considering macropore connectivity; e) mineral map including nanopore connectivity

3.1.6 Lower Tuscaloosa

The SEM BSE image and mineral segmented map of the Lower Tuscaloosa sample are shown in Figures 6a and 6b. Six different minerals are identified, among which quartz is the most dominant phase. Similar to the Bentheimer sample, the sample has a high porosity, about 33% measured from 2D mineral maps. The three types of accessibility maps are shown in Figures 6c, 6d, and 6e. In case of the first approach, the accessibility of quartz is 79.32%, lower than the quartz

265 abundance. Albite and dolomite accessibility agree well with their abundances. K-feldspar and
266 kaolinite accessibilities are higher, where kaolinite accessibility is about 3.5 times higher than the
267 abundance.

268 Considering macropore connectivity reduces the effective porosity to 24% (Figure 6d). The
269 accessibility of quartz, in this case about 83%, which is less than its abundance (Figure 6d).
270 Conversely, the accessibility of kaolinite, the major clay mineral, is 13.41%, significantly higher
271 than its abundance. Taking nanopore connectivity into account makes more areas accessible to
272 fluid (shown in red in Figure 1e) and increases the accessibilities of K-feldspar and dolomite. The
273 effective porosity also increases.

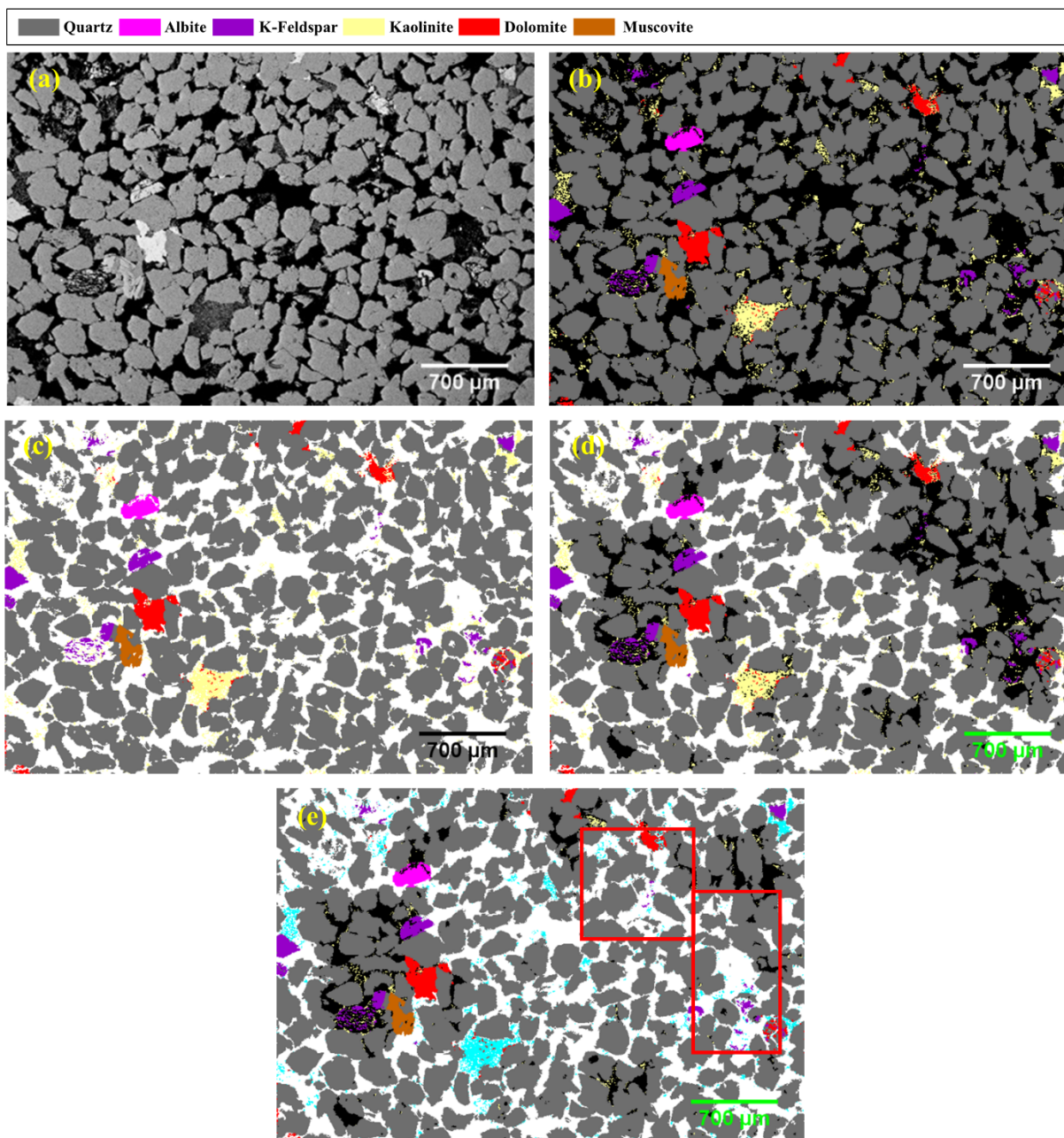


Figure 6: a) 2D SEM BSE image of sample collected from Lower Tuscaloosa formation; b) mineral phase segmented map; c) mineral map considering all macro pore accessible; d) mineral map considering macropore connectivity; e) mineral map including nano pore connectivity

3.1.7 Paluxy

The original and processed images from the Paluxy sandstone are shown in Figures 7 (a and b). Nine minerals are identified in the BSE image, major phases include quartz and albite. The porosity calculated from the BSE image is 19%. When accessibility is determined using the first approach, quartz has lower accessibility than abundance. K-feldspar, albite, calcite, siderite, and muscovite accessibility is slightly larger than their abundances. The two clays, kaolinite and illite have significantly higher accessibilities (16.9% and 2.04%) than their abundances.

Figure 7d presents the mineral map with the macropore connectivity shown in white. In this case, quartz has the highest accessibility, followed by albite and kaolinite. The accessibility of kaolinite is significantly higher than reflected by the abundance of kaolinite. Accessibility values increase for kaolinite, calcite, and illite while they decrease for quartz and albite when nanopore connectivity is considered. Effective porosity determined from macropore and nanopore connectivity approaches are 4.12% and 5.36% respectively, significantly lower than the actual porosity (18.77%).

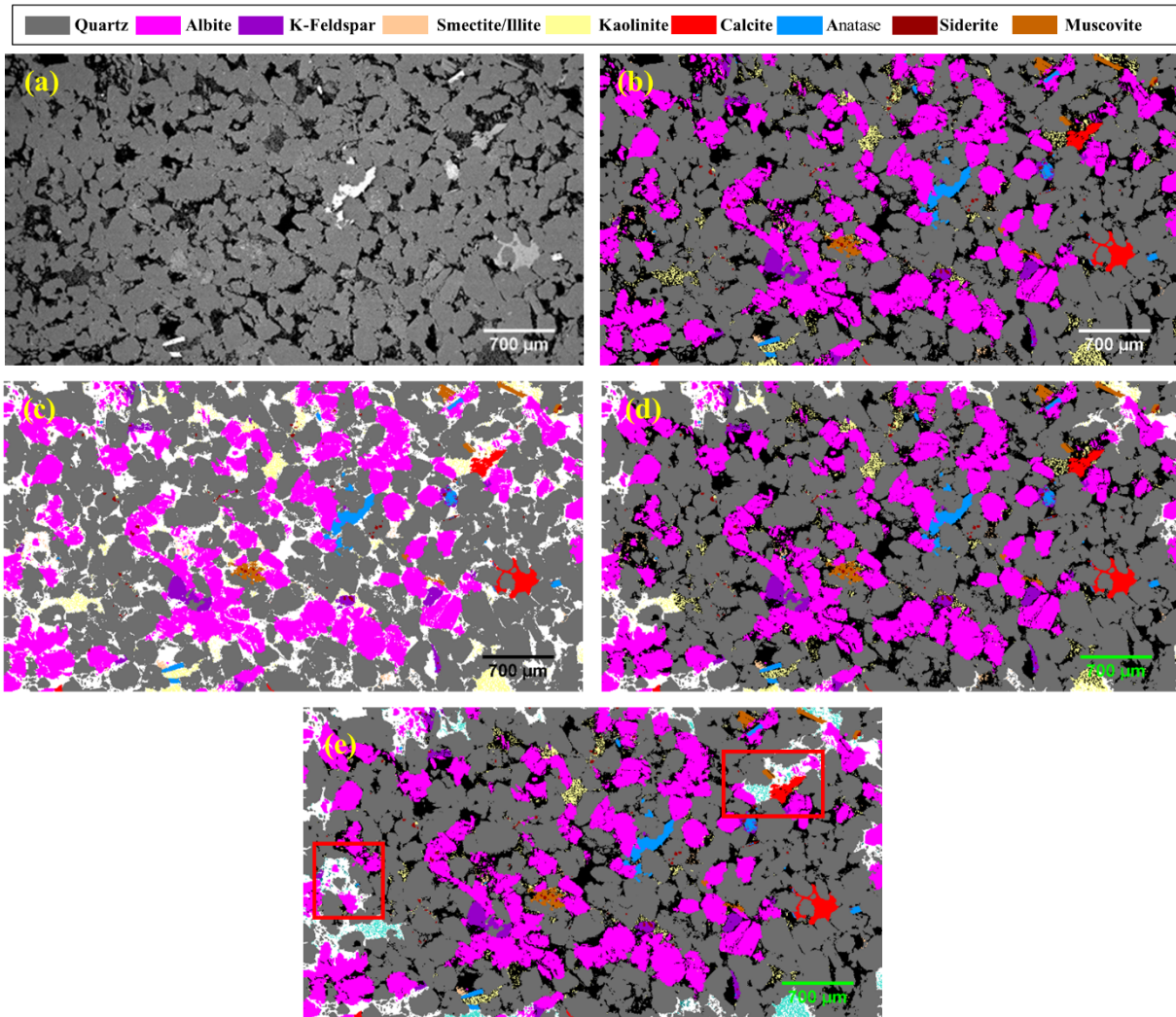


Figure 7: a) SEM BSE image of Paluxy sandstone; b) mineral phase segmented map; c) mineral map considering all macropores accessible; d) mineral map considering macropore connectivity; e) mineral map including nanopore connectivity

3.2 Porosity Comparison

In Figure 8, total porosity and effective porosity are compared for all the samples. Approximately a two to nine times reduction in effective porosity is observed when connectivity is taken into account. The largest drop is evident in the Bandera Gray sample, which has a lower total porosity (15.31%). Consideration of nanopore connectivity increases the effective porosity in

all cases compared to macropore connectivity alone, which is obvious as it reveals more areas for fluid flow. In Figure 8, the Kentucky and Torrey Buff samples have the highest difference between effectivity porosities when nanopores are included, approximately 2.4 times increase. These samples are higher in clay content as compared to the other samples. This is followed by the Bandera Brown sample where effective porosity increases 70% when nanopores are included. The increase in effective porosity include nanopore connectivity for the other samples were all less than a 35% increase.

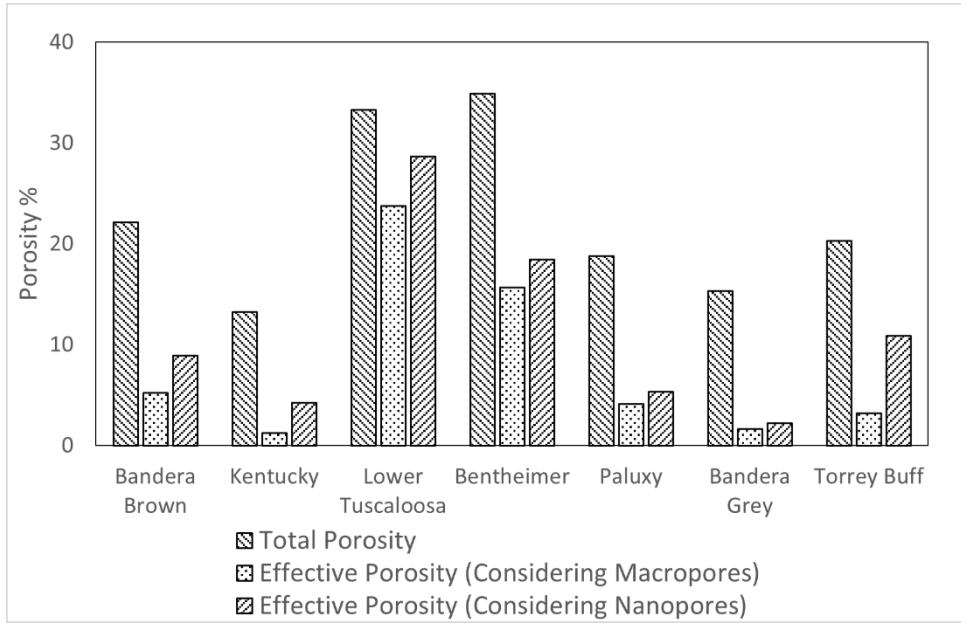


Figure 8: Total porosity and effective porosity comparison for the sandstone samples

3.3 Accessibility Ratio

With the obtained accessibility values from the segmented mineral maps, accessibility ratios are calculated for each mineral. It is calculated by dividing mineral accessibility by mineral abundance for each phase as given by,

$$\text{Accessibility Ratio} = \frac{\text{Mineral Accessibility determined from 2D mineral map \%}}{\text{Mineral Abundance calculated from 2D mineral map \%}}$$

and reported as a unitless number. These ratios provide a normalized reflection of mineral accessibility regardless of mineral quantity for easier comparison among different samples. The value of the ratio being one means that the mineral has the same accessibility as abundance. Accessibility ratios are calculated for quartz, K-feldspar, albite, carbonate, and clay minerals for the three approaches discussed in Section 2.2. If a sample has multiple carbonates or clay minerals, those were combined to reflect total carbonate or clay minerals under a single label for simplicity.

Figure 9 shows the accessibility ratio data for all seven samples. For quartz, the accessibility ratios range from 0.53 to 1.12 for all samples and approaches. For all samples except the Kentucky and Paluxy sample, the range is narrower, 0.75 to 1.12. This indicates that accessibility is relatively well reflected by abundance. For the Kentucky and Paluxy samples, the abundance may not reflect the proportion of quartz that will be available for reaction. Consideration of pore connectivity, both macro, and nanopore, has little effect on accessibility for the Lower Tuscaloosa, Paluxy, and Torrey Buff samples. However, for the Kentucky, Bentheimer, Bandera Brown, and Bandera Gray samples, the accessibility ratios change 22-29% with different connectivity approaches. For most samples, the accessibility ratio increases when macropore connectivity is considered; however, for Kentucky, the ratio decreases by 30% (Figure 9). This sample has the lowest porosity among all samples and also low pore connectivity (Figure 4d).

Larger variations in accessibility ratio are evident between samples and connectivity approaches for K-feldspar. For the Lower Tuscaloosa, Bentheimer, and Paluxy sample, considering all pores connected results in accessibility ratios above 1, which means that the accessibility is higher than the calculated abundance. The assumption of only macropore connectivity significantly impacts calculated accessibility values, reflected by the change in accessibility ratio of 16-87% with the

highest change (87%) occurring for the Kentucky sample. Considering nanopore connectivity increases the accessibility ratio for all samples (0.9-17%) except for the Bandera Gray.

Albite was identified only in five out of seven samples. If all the macropores are considered, the accessibility ratio varies from 0.54 to 1.18. When the connected macropores are accounted for, the largest variation in computed accessibility is for the Lower Tuscaloosa sample (decreases 32%). When macropore and nanopore connectivity is considered, accessibility ratios typically decrease from values considering only connected macropores. The accessibility ratio for the Bandera Brown sample, however, increases by 43% in this case.

Carbonates are present in all samples except the Kentucky sandstone. The two carbonates identified in the samples are calcite and dolomite, which are very common in sandstone samples. The Bentheimer and Bandera Brown samples have very small amounts of carbonates, 0.0003%, and 0.007%, respectively. As a result, when connectivity is considered, the accessibility is zero for these two samples. Torrey Buff has the highest amount of carbonate minerals (25.32% dolomite) but low accessibility, 6.49%, 2.91%, and 2.65% considering all pores, connected macropores, and connected nanopores, respectively. The resulting accessibility ratios are small. Small values are also evident for the Bandera Gray sample where the accessibility is about five times smaller than the abundance. This represents either coating of carbonate grains with clays or carbonates surrounded by other minerals which makes those grains inaccessible to reactive fluids. Conversely, some samples have accessibility ratios greater than one, indicating more of the carbonate minerals are accessible to reactive fluids than reflected by their abundance. Connectivity does largely impact accessibility ratios for some samples. For the Paluxy sample, a seven times increase in accessibility occurs when nanopore connectivity is taken into account.

361 Clay minerals are presented in all samples to varying extents (2.5% to 11.7%). This includes
362 kaolinite, smectite/illite, and chlorite. For clay minerals, the accessibility ratio ranges from 2.66 to
363 as high as 16.26. This is due to clay's characteristic occurrence as grain coatings. When nanopore
364 connectivity is included, an increase in accessibility ratio occurs for all of the samples except the
365 Kentucky sandstone. Comparing the accessibility ratios determined by the three approaches, small
366 variations occur for the Bandera Brown, Kentucky, lower Tuscaloosa, Bandera Gray, and Torrey
367 Buff samples, whereas there are large variations in accessibility ratio with the connectivity
368 approach for Bentheimer and Paluxy samples.

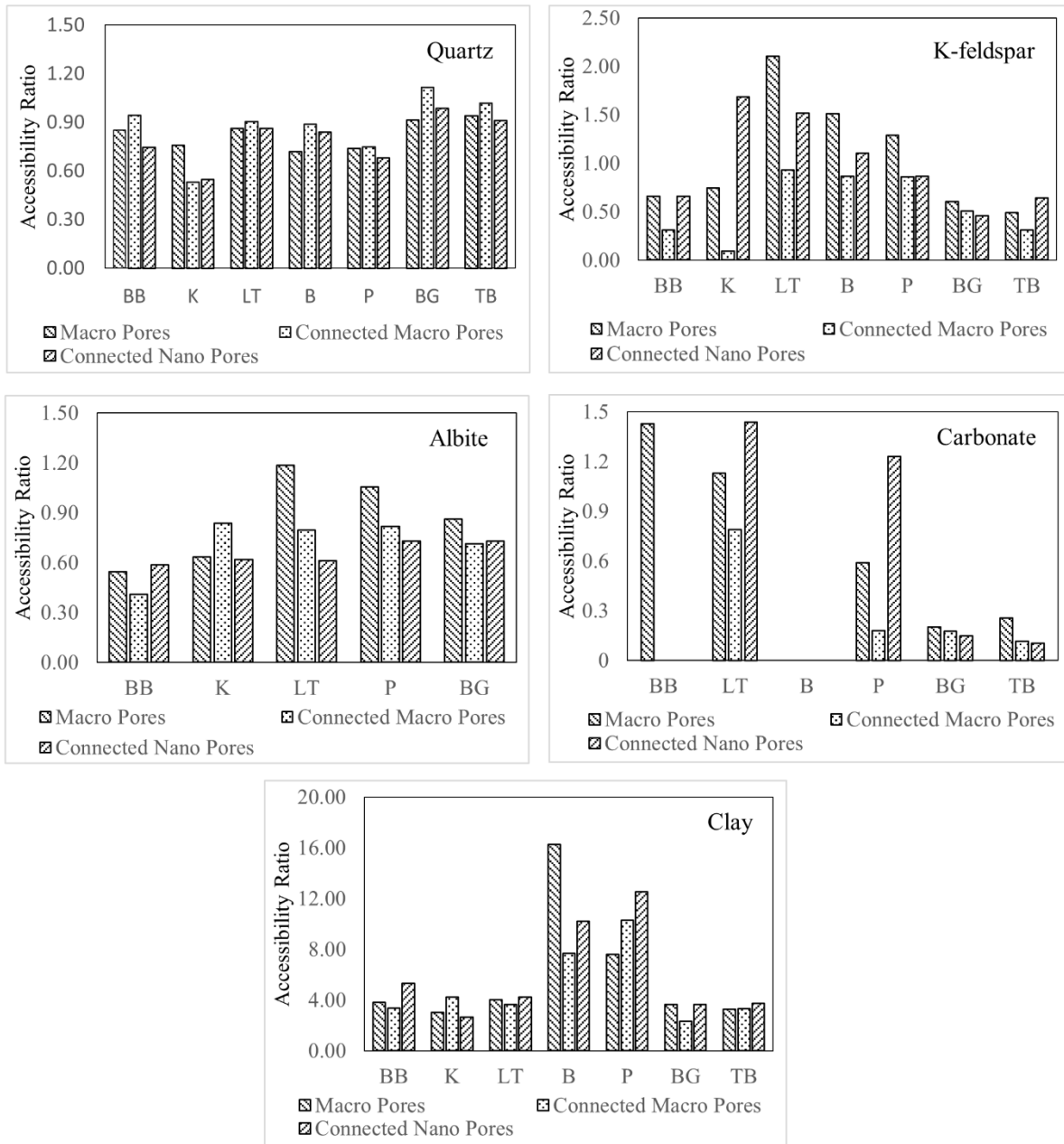


Figure 9: Accessibility ratio comparison for Quartz, K-feldspar, Albite, Carbonate, Clay for all samples

4. Discussion

In this study, we demonstrate the effect of macropore and nanopore connectivity considerations on calculations of mineral accessibility from 2D images. Mineral accessibility was determined

using three approaches for seven sandstone samples. Using 2D SEM BSE image in combination with EDS elementals maps, mineral segmented maps were created for these samples. Accessibility values for quartz, K-feldspar, albite, carbonate, and clay minerals were normalized using their abundances to analyze the differences among the three approaches.

The lowest variations in accessibility ratio were noted for quartz with accessibility ratios ranging from 0.53 to 1.12. Larger variations in accessibility ratios were observed for K-feldspar, albite, and carbonate minerals, ranging from 0.09 to 1.5. This indicates the availability of these phases for reaction may be over (ratios less than 1) or under (ratios greater than one) estimated by their volume fractions. Clay minerals have a large range of accessibility ratios, 2.31 to 16.26, indicating their accessibilities tend to be much higher than their abundance, as was similarly observed in prior literature^{22, 24-26}.

Accessibility is also seen to be impacted by the clay content. When clay minerals are present, they often exist as clay coatings on the major mineral phase's surfaces. As a result, the accessibility ratios for other phases will be lower. For example, the accessibility ratio for quartz in the Kentucky sample, which had the highest clay content, was the lowest among all samples considered.

Large variations in accessibility occurred for some mineral phases when nanopore connectivity was considered. Increases in accessibility as high as 17 times estimates considering only macropore connectivity were observed for K-feldspar in the Kentucky sample when nanopore connectivity was taken into consideration. Interestingly, these large variations were not reflected in other mineral phases in the sample where the accessibility of quartz, for example, had little variation when connected macropores and connected nanopores were considered. Large variations in effective porosity are also evident for different approaches to considering pore connectivity. These variations, however, are not always reflected by variations in mineral accessibility. The

effective porosity of the Bandera Gray sample is significantly reduced when considering pore connectivity but little variation in calculated mineral accessibilities occurs.

In terms of predicting reactivity, it is most critical to understand the accessibility of carbonate phases as they often have the fastest reaction rates, e.g. in geologic CO₂ sequestration systems. The accessibility ratios for carbonates in the Bandera Gray and Torrey Buff samples are less than 0.3, reflecting low accessibility as compared to abundance. These samples have the highest fraction of carbonate phases, 5.69%, and 25.32%, respectively. As carbonate phases tend to exist as cement between mineral phases, it is anticipated they will have an accessibility ratio of less than one. Higher accessibilities of carbonate phases are observed in the other samples, but these samples all have low fractions of carbonate minerals <1.5% such that it is challenging to make conclusive ties to the accessibility of these phases.

5. Conclusion

In this work, we enhance understanding of mineral accessibility in sandstone samples, to improve understanding of the physical properties of porous materials and ultimately improve modeling reactive transport simulations by better characterizing sample reactivity. Mineral accessibility reflects the availability of minerals for reaction with reactive fluids as is often not considered in reactive transport simulations but may help explain discrepancies with observed field scale reaction rates.

Accuracy of reactive transport modeling, for simulating geologic storage of CO₂ or other applications as discussed in the introduction, largely depends on the precise determination of mineral reaction rates. Excluding the consideration of pore connectivity may provide imprecise estimates of reactivity, mineral reactive surface areas, and thus simulated mineral reaction rates which are directly proportional to reactive surface area. Reactivity may be reduced if grains

surfaces are concealed by clay minerals or inaccessible due to presence as a grain inclusion²⁴. The nanoscale connectivity through thin channels of clay minerals in sandstone samples should also be taken into consideration as it may impacts estimates of surface area of certain minerals covered with those clays^{22,26}. This was observed in recent work which noted reaction rates in flow-through dissolution experiments were effectively simulated accounting for accessibility via connected nano and macropores and rates over estimated assuming all mineral phases were accessible²².

The mineral abundances and accessibilities determined using three approaches for seven sandstone samples reveal the discrepancy between abundance and accessibility. To explore the variation in accessibilities of a particular mineral in different samples, associated accessibility ratios were calculated. As shown in Figure 9, accessibility ratios for K-feldspar, albite and carbonate range within 1.5, while clay minerals have a larger range which agrees well with Peters (2009)²⁴. While useful for comparing the impact of these three approaches, these ratios also have utility for adjusting mineral reactive surface areas in reactive transport simulations to account for variations in accessibility. For example, an accessible mineral surface area could be obtained by multiplying the specific surface area of a given mineral phase (often obtained from the Brunner-Emmett-Teller (BET) method) by the accessibility ratio.

Recent reactive transport modeling work considered implications of variations in surface area on simulated mineral reaction rates and noted little variation in simulation results when surface areas varied within one order of magnitude, as resulting from accessible surface areas determined from images with different resolution^{25,31}. As such, some of the variations in accessibility (within one order of magnitude) observed here for different pore connectivity approaches are not anticipated to largely impact simulated mineral reactions or reaction rates. Observed variations in accessibility for clay and carbonate minerals, however, may be important. Due to its fast reaction

rate, differences in carbonate mineral accessibility are only anticipated to impact simulation reactions on short time scales (hours to days) where even large differences in calcite surface area values were insufficient in terms of the overall simulation results at long time scales (years) in Qin and Beckingham (2021)³¹. Clay mineral accessibility determined here varies up to one order of magnitude so larger impacts in simulated associated reaction rates may occur. Due to the slower reaction rate of these phases, this is anticipated to impact only longer simulated time scales (years) but will likely not be significant for simulations interested in short time scales (hours to days)³¹.

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Supporting Information Available

- SEM BSE image properties of each sample
- Mineral accessibility determined using the three approaches for all samples

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