Supporting Information For
Oedometric Small-Angle Neutron Scattering: *In Situ* Observation of Nano-Pore Structure During Bentonite Consolidation and Swelling in Dry and Hydrous CO_2 Environments

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Number of pages: 69

Number of figures: 30 main figures labeled S1-S30, with several other figures embedded in a finite element analysis report

Number of tables: no main tables, with several tables embedded in a finite element analysis report

This Supporting Information contains: information on the design, construction, and finite element testing of components of both the Titanium oedometric cell (TOC) and the Oedometric SANS Cell (OSC); design elements of the OSC to minimize multiple scattering; information on interpretation of SANS results including sensitivity to parameter choices; and results of TOUGH2 simulations used to calculate water saturation in liquid CO2 at experimental conditions.

Contents

S1. Design, Construction, and Testing of Oedometric Cells Used in the Study

S1.1. Design and Materials of the Aluminum-window Oedometer

The aluminum oedometer has a sample geometry such that it is optimized for the optics of small-angle neutron scattering methods (this includes aluminum windows or so-called "neutron windows" as shown in Figure 1). The oedometer was leak and overpressure tested at Sandia National Laboratories' (SNL's) Geomechanics Laboratory to determine the maximum allowable working pressure (MAWP) and the safety factor for this custom built oedometer. The oedometer contains a 0.050 to 0.100 in^3 sample chamber, depending on position of the compression piston. The sample chamber is for placement of clay or other geological samples under uniaxial strain with pore fluids. The oedometer design facilitates measurement of "swelling" pressure or sample compaction. The oedometer is composed of steel and aluminum. The aluminum portion for the sample chamber has suitable low neutron attenuation to allow for measurement of a sample's neutron scattering properties to infer pore structure. Thus, in addition to swelling-pressure measurements, the oedometer is designed for use in neutron-beam studies. The sample thickness normal to the neutron beam is ~3.2 mm, which is large enough to permit measurements of consolidation but small enough to minimize effects of multiple neutron scattering. The piping system connected to the OSC is compatible with the piping system described in the main text that was developed for the TIOC described below, except that different pressure relief valves (PRFs) are needed that are set at a lower pressure. All o-rings are composed of ethylene propylene (EP) or ethylene propylene diene monomer (EPDM) and thus resistant to supercritical CO_2. Precision Plastic Mesh is used at the top and bottom of the clay sample to serve as a porous frit. The oedometer design includes a narrow slot for the sample, with a narrow piston. The pressure applied by the hydraulic piston will result in approximately

7.74 times higher stress on the sample due to the reduction of surface area of the ram piston that contacts the sample.

Figure S1 presents a schematic of the oedometer with annotation regarding fluid inlets and/or outlets, sample location, and dimensions. Results of a leak and overpressure test, safety-related information, and a finite element analysis on this custom-built vessel follow below.

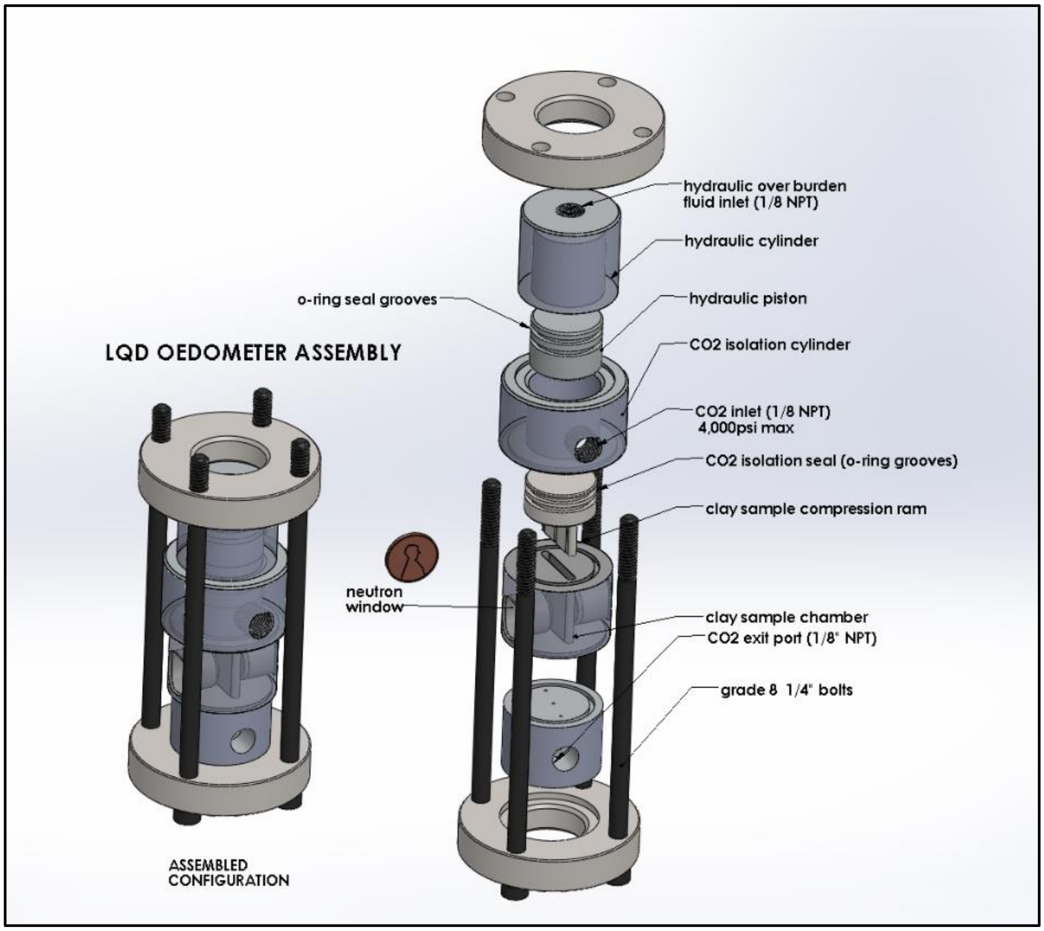


Figure S1. Schematic diagram of OSC with annotation indicated by arrows. Note penny for scale.

The Al-window oedometer required testing to determine the MAWP for the unique geometry and to verify no leaks. This testing used overpressure testing to determine the MAWP, the value to set the PRVs, and the factor of safety. For overpressure testing, strain gauges were placed at

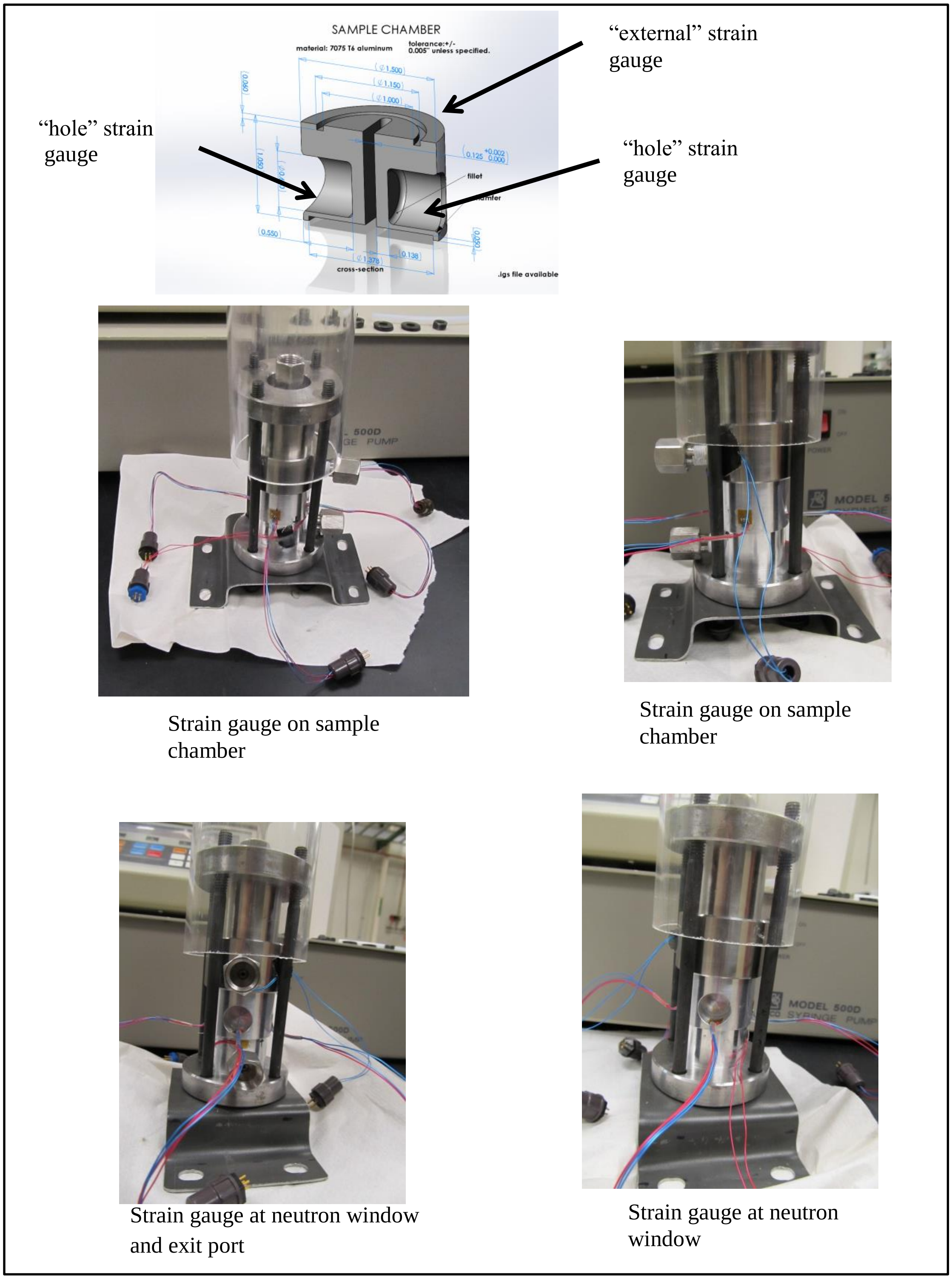


Figure S2. Strain gauge mounting locations used for overpressure testing of the OSC.

five locations: two on the clay sample chamber at the location where the internal chamber comes closest to the outside wall; two at the base of the neutron window; and one above the CO_2 exit port (see Figure S2 for mounting locations).

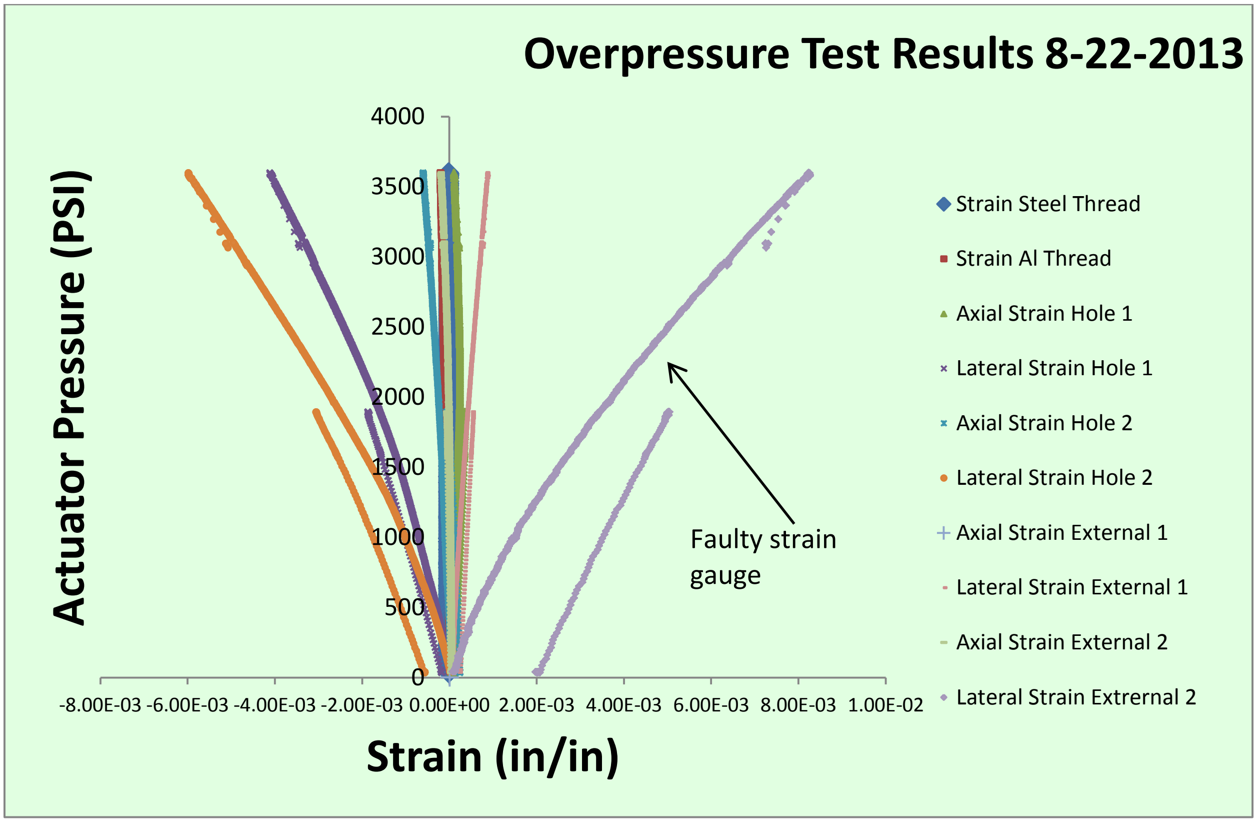


Figure S3. Results of pressure test to approximately 3673 psi.

During overpressure testing shown in Figure S3, fluid was placed in both the hydraulic cylinder and sample chamber. Pressure was increased inside the sample chamber. The test was performed with the vessel behind a Lexan barrier. The NPT fitting below the sample chamber leaked while pressure was applied, and thus it was retaped with Teflon and then did not leak. Pressure was increased to approximately 3598 psi and 3673 psi, respectively, for the hydraulic piston and within the sample chamber. Thus, the overpressure went to 1.22 (3673/3000) of 3,000 psi. The approximately highest pressure was held for approximately 10 minutes.

The overpressure test was meant to achieve approximately 3,900 psi based on an original intended MAWP of 3000 psi (based on initial FEA that used even higher internal pressure; see finite element analysis below). However, the maximum pressure achieved in the sample chamber was ~3673 psi. Pressure and strain gauge data are shown in Figure S3. Note that the “Lateral Strain External 2” was faulty and the data should be ignored. The sample chamber is made of 7075 T6 Aluminum. For this aluminum, the yield strain is ~0.7% (see Oskouei and Ibrahim, 2011). The orange curve “Lateral Strain Hole 2” shows a strain of -0.6% at 3,600 psi, which is the maximum observed strain. Extrapolating from the orange curve on Figure S3 to obtain the yield at 0.7% strain, we obtain a corresponding pressure of 4,000 psi. If we use a Factor of Safety of 4 and ignore any effects of geometry and also ignore any fatigue effects of the aluminum, that brings us to an operating pressure of 4,000/4 = 1,000 psi. Thus, the MAWP is set to 1,000 psi, with PRV. The operating pressure was determined to be from 0 to approximately 950 psi. The vessel showed no visible leakage when taken to the highest pressure.

This Al-window oedometer is to only be operated while it is behind Lexan shielding. Lexan shielding includes a tube around the oedometer, and a Lexan box around the entire system. Calculation on stored energy show that the oedometer itself has less stored energy than a basketball, for conditions at high pressure (3,000 psi); our tests are performed at a much lower MAWP. Pressure sources for the oedometer include fluid inlet and outlets to the sample chamber, and the fluid port for the upper hydraulic load cell (see Figure S2). As just discussed, the MAWP of the oedometer system is 1,000 psi. This MAWP is 2,000 psi lower that the original Ti odeomter (see the discussion on the Ti oedometer below). Thus, when using this Al-window oedometer, the PRVs must be set to 1,000 psi. The load cell is connected to a HiP pressure generator or ISCO pump, which is described in the piping system data package (not given here). The operating pressure for the piping system to the sample chamber is from 0 –950 psi. The HiP pressure generator pressure, along with the sample swelling pressure, has a PRV also set to 1,000 psi. Thus, the PRV information here should be used for the piping system (in a different PSDP) when using this Al-steel oedometer.

S1.2. Finite Element Analysis of the OSC

The SolidWorks finite element analysis (FEA) report as prepared by co-author Mark Taylor is given in this section by component. This includes preliminary Factor-Of-Safety determinations by component shown in Figure 1, including the: A. hydraulic cylinder (ram); B. the pore pressure (CO_2) isolation cylinders; and C. the sample (clay) chamber including the aluminum hydraulic windows.

A. FE Simulation of Oedometer Hydraulic Cylinder Deformation

Date: Tuesday, July 30, 2013
Designer: M.Taylor

Study name: hydraulic chamber for oedometer

Analysis type: Static

Description

This report contains detailed information from a finite element stress analysis performed on the hydraulic cylinder, a part of the Los Alamos designed oedometer from July of 2013. A Solidworks FEA stress analysis was performed using the Solidworks Simulation software. In this study, the model was subjected to a simulated 4,000 psi hydrostatic load on all pressure exposed surfaces.

Conclusion

The stated minimum factor of safety is reported at 5.3, though it is evident from the stress map and the FOS map, this stress level is only found at one spot on an internal surface that is blanketed by layers of lower stressed material. The functional minimum FOS is measured by the stresses on the external walls of the vessel that would have to rupture in order for a failure to occur. By that measure the minimum factor of safety appears to be >7.

Model Information

Model name: Oedometer Hydraulic Cylinder
Current Configuration: Default

Solid Bodies			
Document Name and Reference	Treated As	Volumetric Properties	Document Path/Date Modified
Cut-Sweep2 	Solid Body	Mass:0.136512 kg Volume:1.7064e-005 m^3 Density:8000 kg/m^3 Weight:1.33781 N	C:\Users\149306\Desktop\Solidworks 2013\Oedometer Project\Oedometer Hydraulic Cylinder.SLDPRT Jul 25 09:20:20 2013

Study Properties

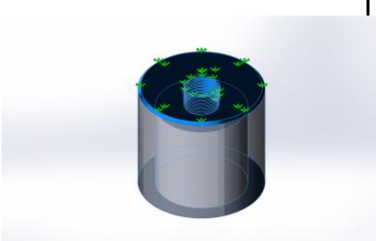
Study name	hydraulic chamber for oedometer
Analysis type	Static
Mesh type	Solid Mesh
Thermal Effect:	On
Thermal option	Include temperature loads
Zero strain temperature	298 Kelvin
Include fluid pressure effects from SolidWorks Flow Simulation	Off
Solver type	FFEPlus

Inplane Effect:	Off
Soft Spring:	Off
Inertial Relief:	Off
Incompatible bonding options	Automatic
Large displacement	Off
Compute free body forces	On
Friction	Off
Use Adaptive Method:	Off
Result folder	SolidWorks document (C:\Users\149306\Desktop\Solidworks 2013\Oedometer Project)

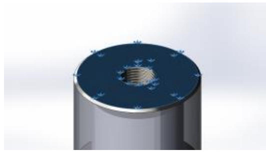
Units

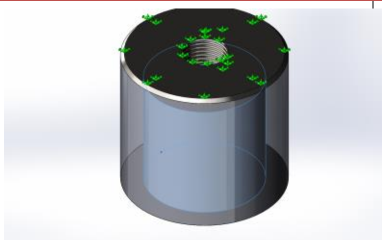
Unit system:	SI (MKS)
Length/Displacement	mm
Temperature	Kelvin
Angular velocity	Rad/sec
Pressure/Stress	N/m^2

Material Properties

Model Reference	Properties	Components
	Name: **AISI 316 Stainless Steel Sheet (SS)** Model type: **Linear Elastic Isotropic** Default failure criterion: **Max von Mises Stress** Yield strength: **25000 psi** Tensile strength: **84121.9 psi** Elastic modulus: **2.79923e+007 psi** Poisson's ratio: **0.27** Mass density: **0.289018 lb/in^3** Thermal expansion coefficient: **8.88889e-006 /Fahrenheit**	**SolidBody 1(Cut-Sweep2)(Oedometer Hydraulic Cylinder)**
Curve Data:N/A		

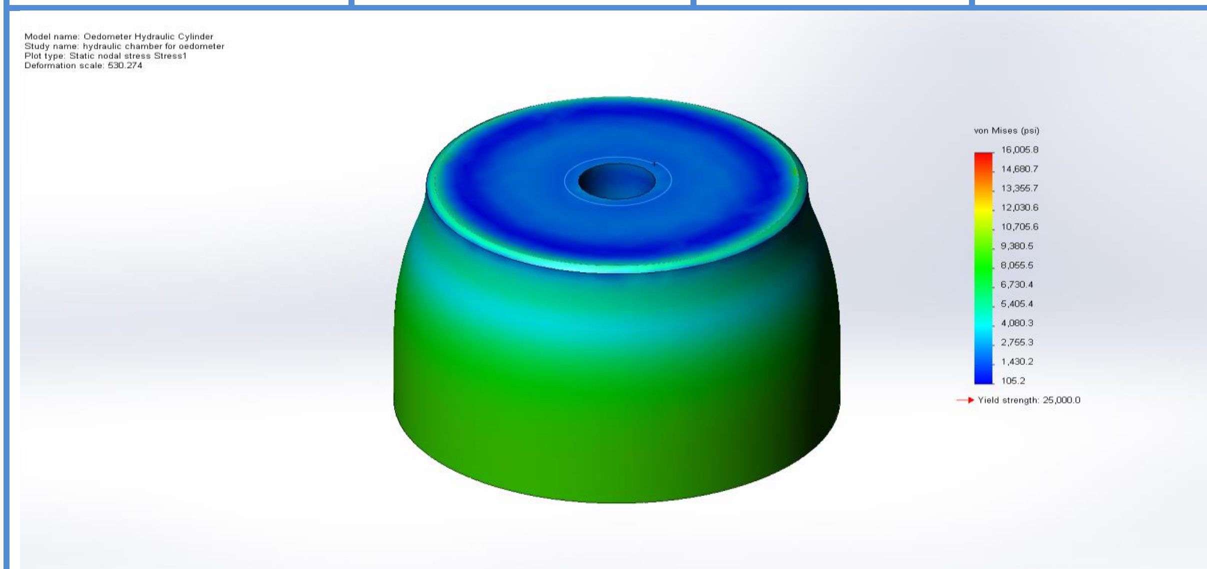
Loads and Fixtures

Fixture name	Fixture Image	Fixture Details	
Fixed-1		**Entities:** **Type:**	**1 face(s)** **Fixed Geometry**

Load name	Load Image	Load Details	
Pressure-1		**Entities:** **Type:** **Value:** **Units:**	**1 face(s)** **Normal to selected face** **4000** **psi**

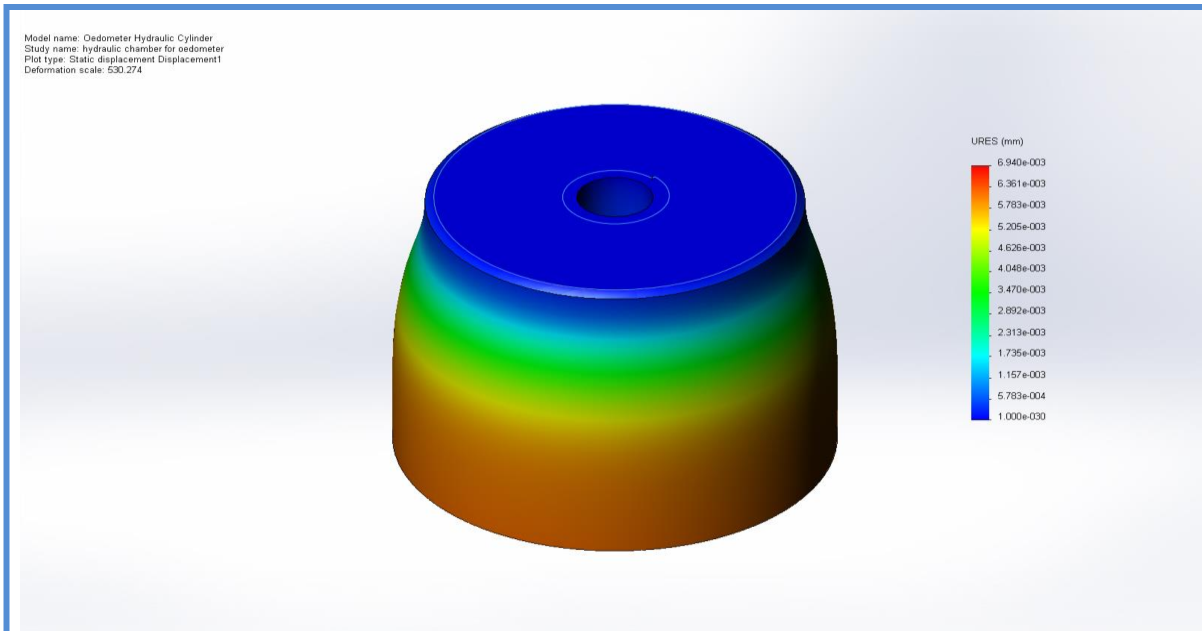
Study Results

Name	Type	Min	Max
Stress1	VON: von Mises Stress	105.161 psi Node: 935	16005.8 psi Node: 233



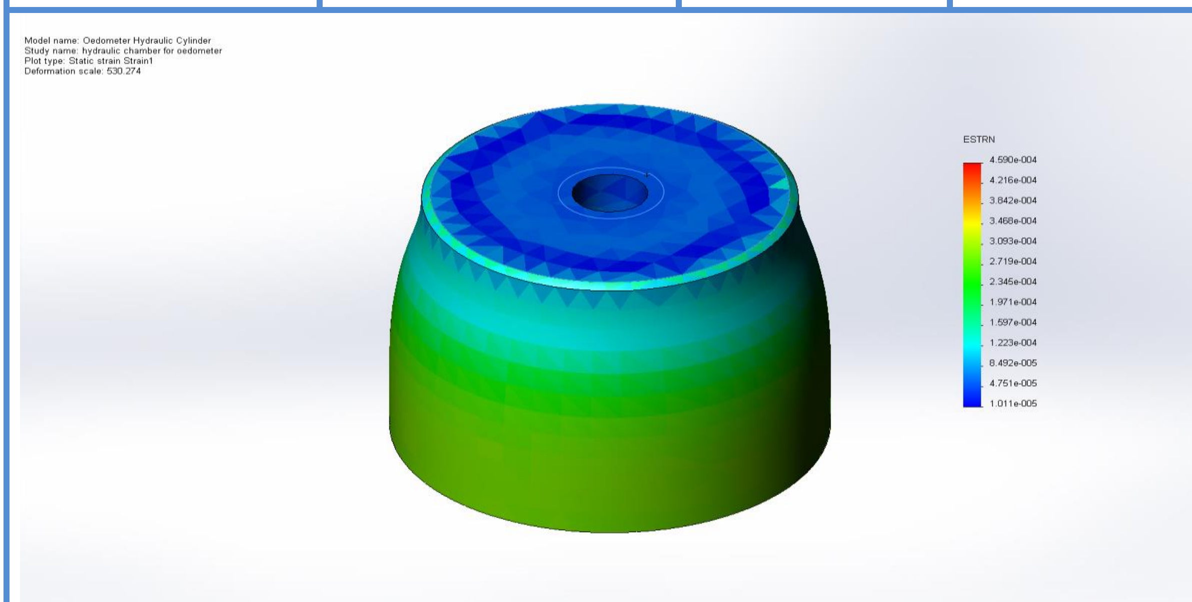
Oedometer Hydraulic Cylinder-hydraulic chamber for oedometer-Stress-Stress1

Name	Type	Min	Max
Displacement1	URES: Resultant Displacement	0 mm Node: 236	0.00693973 mm Node: 11718



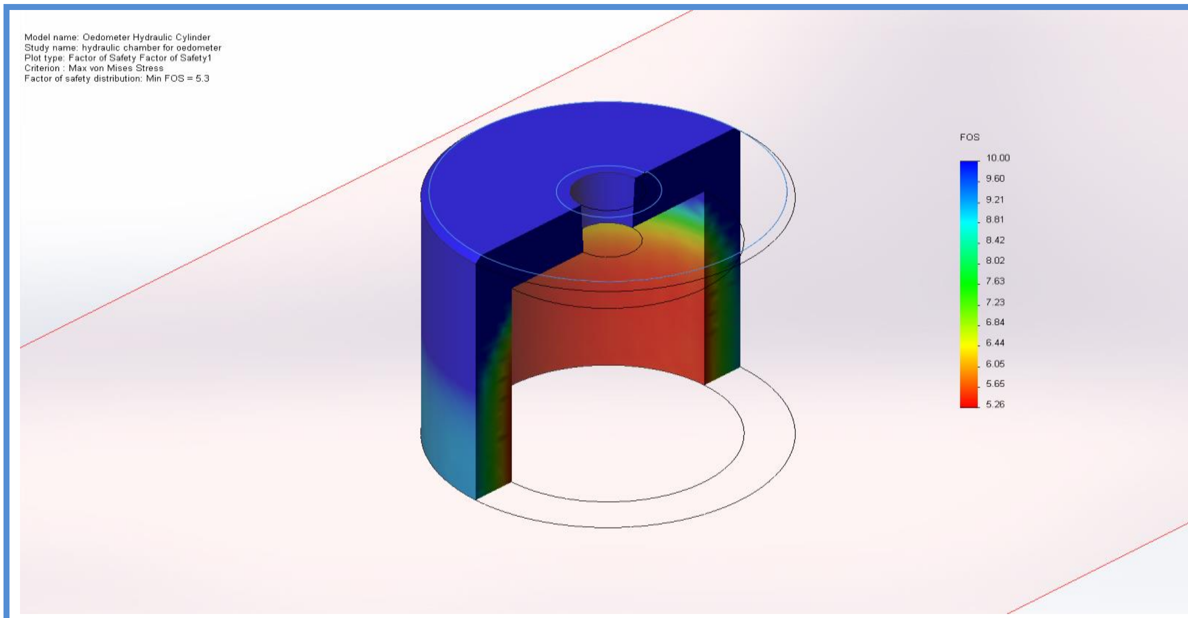
Oedometer Hydraulic Cylinder-hydraulic chamber for oedometer-Displacement-Displacement1

Name	Type	Min	Max
Strain1	ESTRN: Equivalent Strain	1.01087e-005 Element: 2577	0.000458968 Element: 5076



Oedometer Hydraulic Cylinder-hydraulic chamber for oedometer-Strain-Strain1

Name	Type	Min	Max
Factor of Safety1	Max von Mises Stress	5.25573 Node: 233	799.938 Node: 935



Oedometer Hydraulic Cylinder-hydraulic chamber for oedometer-Factor of Safety-Factor of Safety1

B. Simulation of CO2 cylinder for Porous Media Ram.

Date: Tuesday, July 30, 2013

Designer: M. Taylor

Study name: CO2 chamber study

Analysis type: Static

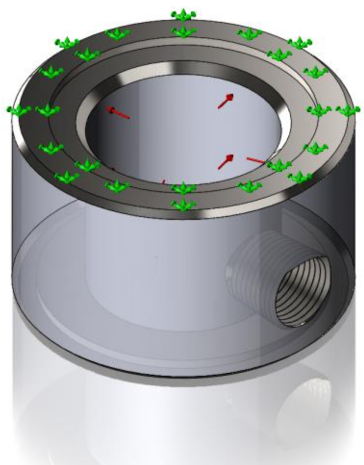
Description

This report contains detailed information from a finite element stress analysis performed on the porous media ram cylinder, a part of the Los Alamos designed oedometer from July of 2013. A Solidworks FEA stress analysis was performed using the Solidworks Simulation software. In this study, the model was subjected to a simulated 4,000 psi hydrostatic load on all pressure exposed surfaces.

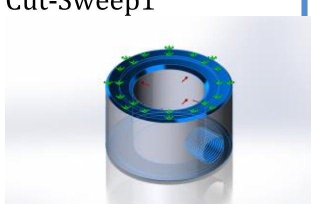
Conclusion

Although the stated minimum factor of safety is reported at 2.3, though it is evident from the stress map, this stress level is only found at one spot on an internal surface that is blanketed by layers of lower stressed material. The functional minimum FOS is measured by the stresses on the external walls of the vessel that would have to rupture in order for a failure to occur. By that measure the minimum factor of safety appears to be >6.

Model Information



Model name: CO2 cylinder for ram
Current Configuration: Default

Solid Bodies			
Document Name and Reference	Treated As	Volumetric Properties	Document Path/Date Modified
Cut-Sweep1 	Solid Body	Mass:0.205309 kg Volume:2.55773e-005 m^3 Density:8027 kg/m^3 Weight:2.01203 N	C:\Users\149306\Desktop\Solidworks 2013\Oedometer Project\CO2 cylinder for ram.SLDPRT Jul 25 08:40:33 2013

Study Properties

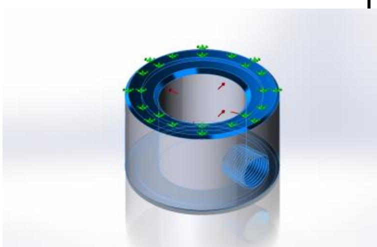
Study name	CO2 chamber study

Analysis type	Static
Mesh type	Solid Mesh
Thermal Effect:	On
Thermal option	Include temperature loads
Zero strain temperature	298 Kelvin
Include fluid pressure effects from SolidWorks Flow Simulation	Off
Solver type	FFEPlus
Inplane Effect:	Off
Soft Spring:	Off
Inertial Relief:	Off
Incompatible bonding options	Automatic
Large displacement	Off
Compute free body forces	On
Friction	Off
Use Adaptive Method:	Off
Result folder	SolidWorks document (C:\Users\149306\Desktop\Solidworks 2013\Oedometer Project)

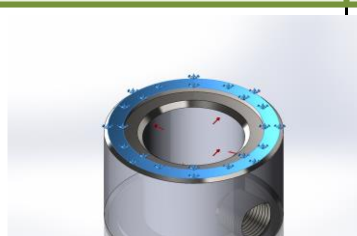
Units

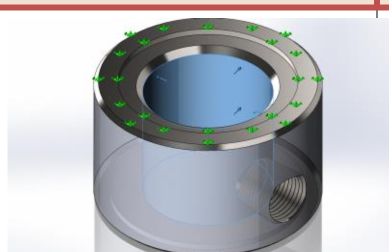
Unit system:	SI (MKS)
Length/Displacement	mm
Temperature	Kelvin
Angular velocity	Rad/sec
Pressure/Stress	N/m^2

Material Properties

Model Reference	Properties	Components
	Name: **AISI Type 316L stainless steel** Model type: **Linear Elastic Isotropic** Default failure criterion: **Max von Mises Stress** Yield strength: **1.7e+008 N/m^2** Tensile strength: **4.85e+008 N/m^2** Elastic modulus: **2e+011 N/m^2** Poisson's ratio: **0.265** Mass density: **8027 kg/m^3** Shear modulus: **8.2e+010 N/m^2** Thermal expansion coefficient: **1.65e-005 /Kelvin**	**SolidBody 1(Cut-Sweep1)(CO2 cylinder for ram)**
Curve Data:N/A		

Loads and Fixtures

Fixture name	Fixture Image	Fixture Details
Fixed-1		**Entities:** **1 face(s)** **Type:** **Fixed Geometry**

Load name	Load Image	Load Details
Pressure-1		**Entities:** **1 face(s)** **Type:** **Normal to selected face** **Value:** **4000** **Units:** **psi**

Mesh Information

Mesh type	Solid Mesh
Mesher Used:	Curvature based mesh
Jacobian points	4 Points
Maximum element size	0 in

Minimum element size	0 in
Mesh Quality	High

Resultant Forces

Reaction Forces

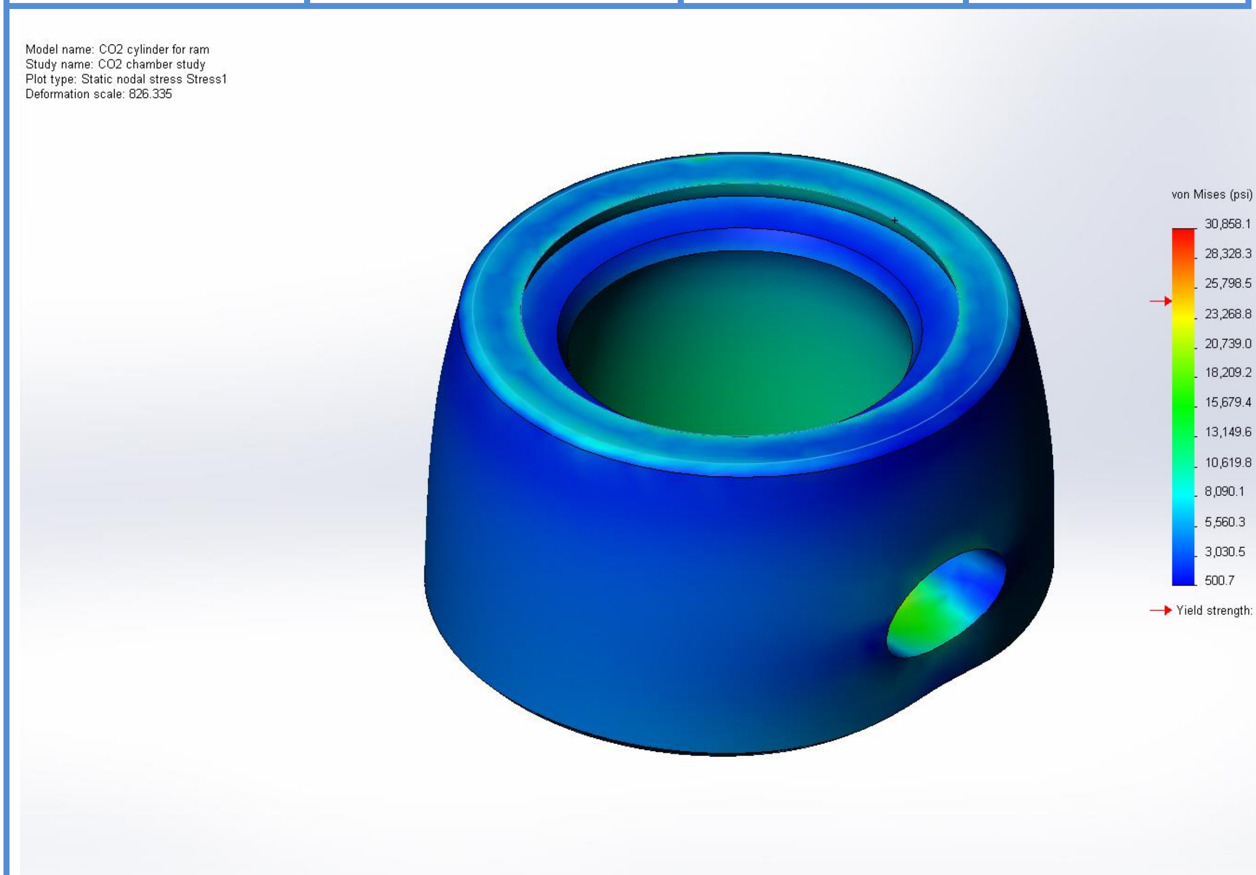
Selection set	Units	Sum X	Sum Y	Sum Z	Resultant
Entire Model	N	1632.02	-0.0420494	0.00940323	1632.02

Reaction Moments

Selection set	Units	Sum X	Sum Y	Sum Z	Resultant
Entire Model	N-m	0	0	0	0

Study Results

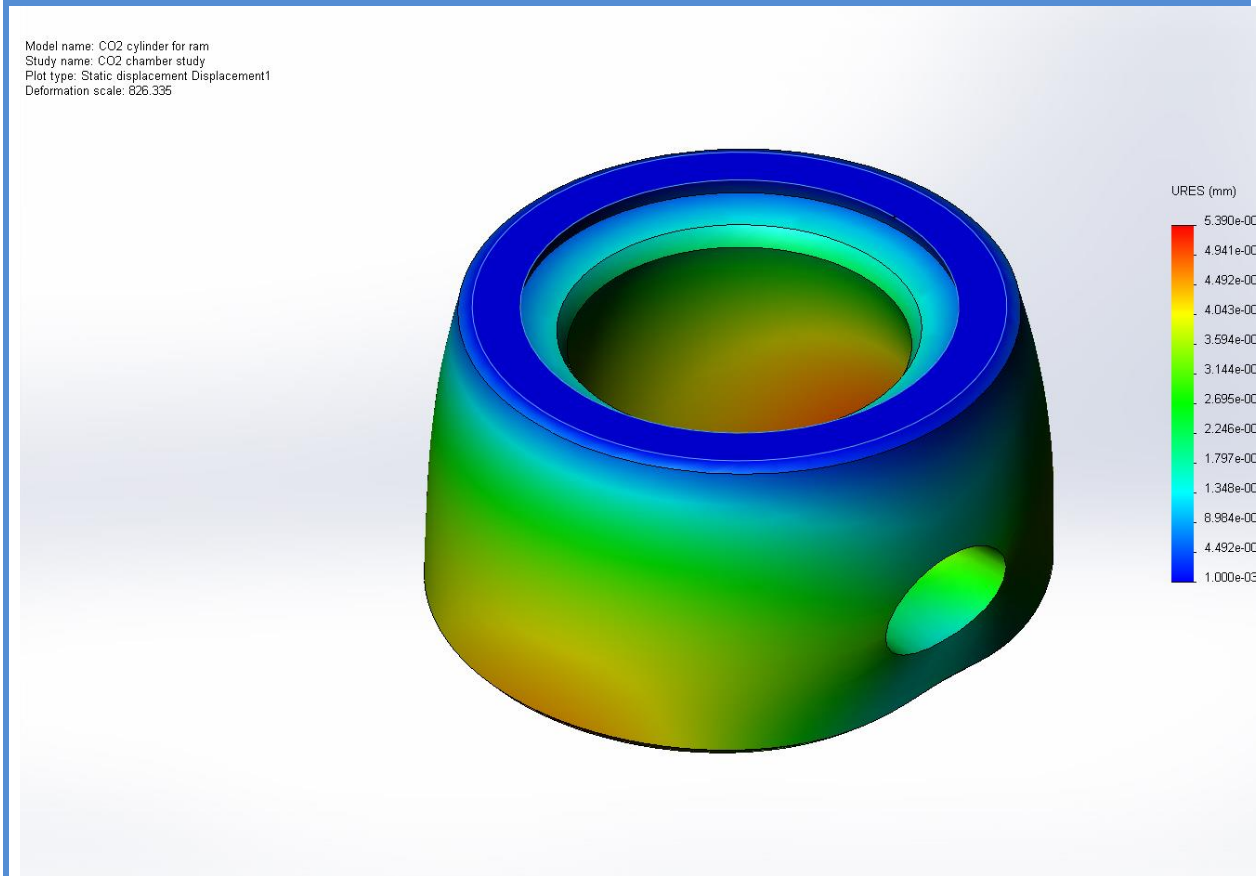
Name	Type	Min	Max
Stress1	VON: von Mises Stress	500.722 psi Node: 14896	30858.1 psi Node: 220



CO2 cylinder for ram-CO2 chamber study-Stress-Stress1

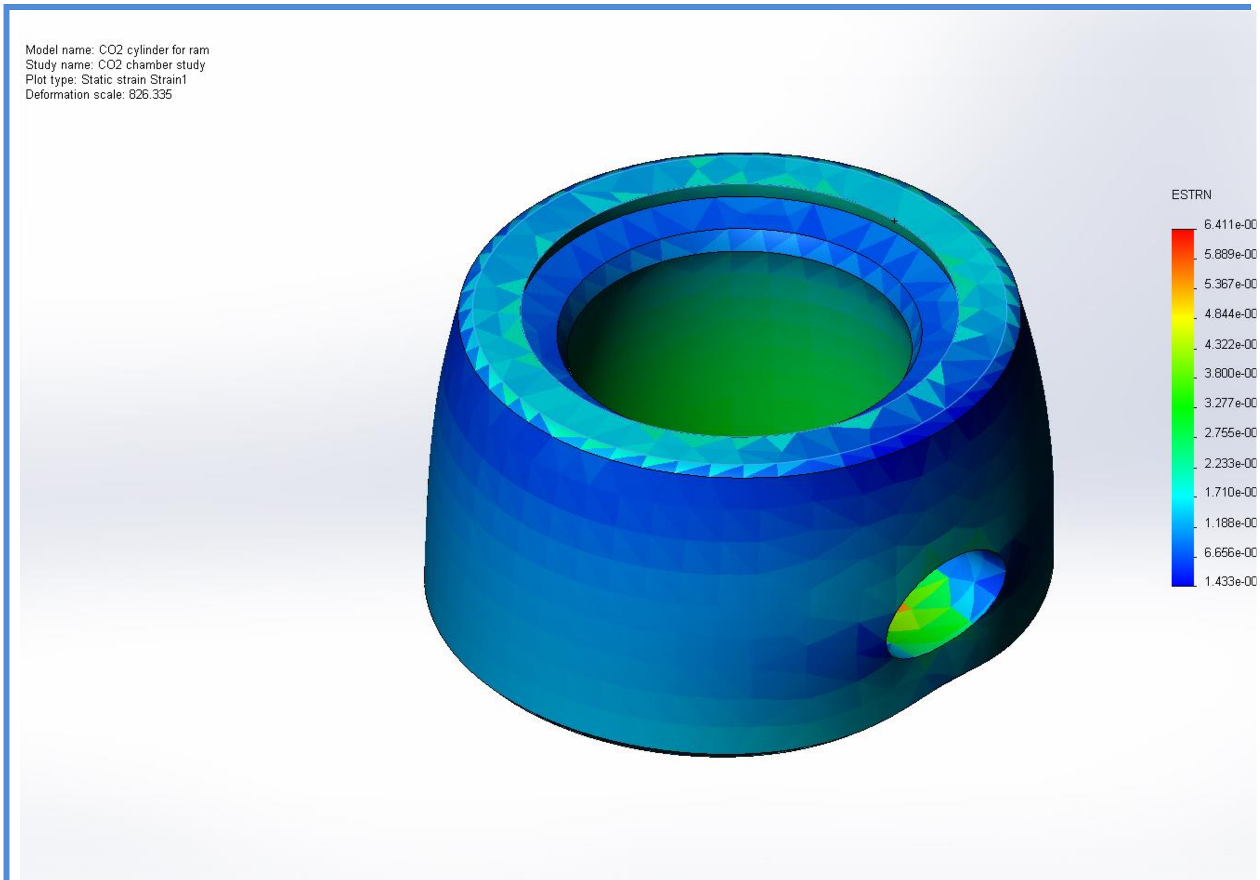
Name	Type	Min	Max

Displacement1	URES: Resultant Displacement	0 mm Node: 1	0.0053904 mm Node: 945



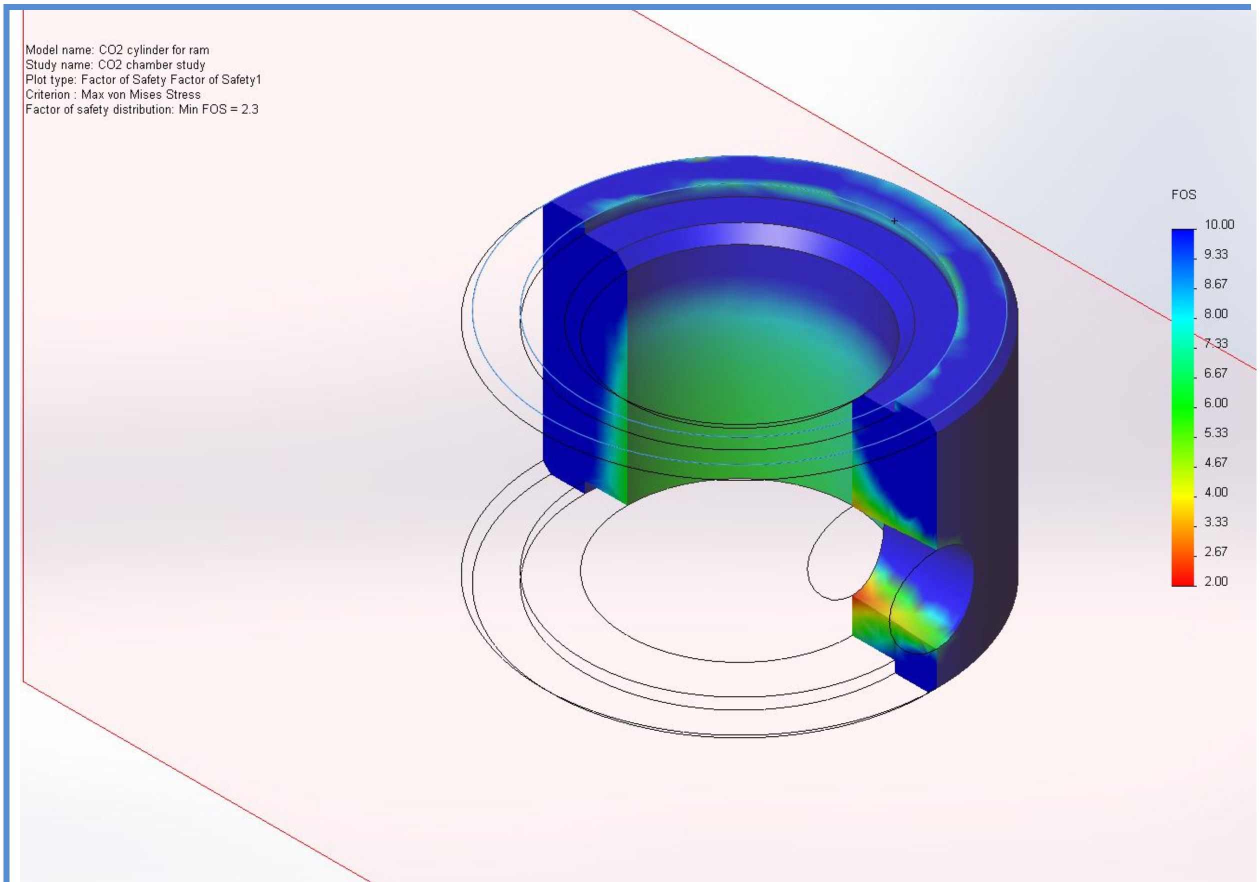
CO2 cylinder for ram-CO2 chamber study-Displacement-Displacement1

Name	Type	Min	Max
Strain1	ESTRN: Equivalent Strain	1.43285e-005 Element: 7154	0.000641117 Element: 4797



CO2 cylinder for ram-CO2 chamber study-Strain-Strain1

Name	Type	Min	Max
Factor of Safety1	Max von Mises Stress	2.27957 Node: 220	140.484 Node: 14896



CO2 cylinder for ram-CO2 chamber study-Factor of Safety-Factor of Safety1

C. Stress Simulation of Oedometer sample holder and neutron windows

Date: Tuesday, July 30, 2013
Designer: M. Taylor
Study name: Sample chamber study
Analysis type: Static

Description

The sample chamber of the Los Alamos designed oedometer proposed in July of 2013 was designed in Solidworks and an FEA stress analysis was performed using the Solidworks Simulation software. In this study, the model was subjected to a simulated 4,000 psi hydrostatic load on all pressure exposed surfaces.

Conclusion

Although the stated minimum factor of safety is reported at 2.1, it is evident that this stress level is only found on internal surfaces that are blanketed by layers of lower stressed material. The actually minimum should be measured by the stresses on the external walls of the vessel that would have to rupture in order for a failure to occur. By that measure the minimum factor of safety appears to be >6.

Model Information

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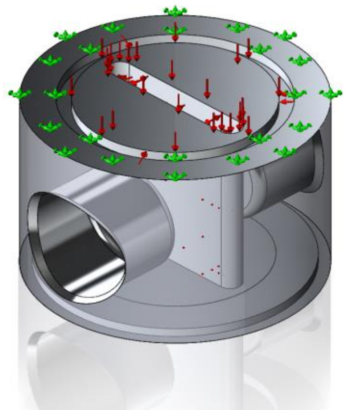
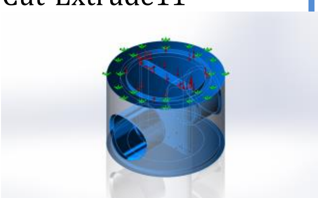
<tr><td colspan="4">
Model name: Oedometer sample holder
Current Configuration: Default</td></tr>
<tr><td colspan="4">Solid Bodies</td></tr>
<tr><td>Document Name and Reference</td><td>Treated As</td><td>Volumetric Properties</td><td>Document Path/Date Modified</td></tr>
<tr><td>Cut-Extrude11
</td><td>Solid Body</td><td>Mass:0.0643858 kg
Volume:2.29131e-005 m^3
Density:2810 kg/m^3
Weight:0.630981 N</td><td>C:\Users\149306\Desktop\Solidworks 2013\Oedometer Project\Fabrication folder for Oedometer\Oedometer sample holder.SLDPRT
Jul 30 09:14:58 2013</td></tr>
</table>

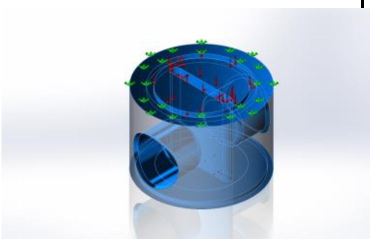
Study Properties

Study name	Sample chamber study
Analysis type	Static
Mesh type	Solid Mesh
Thermal Effect:	On
Thermal option	Include temperature loads
Zero strain temperature	298 Kelvin
Include fluid pressure effects from SolidWorks Flow Simulation	Off
Solver type	FFEPlus
Inplane Effect:	Off
Soft Spring:	Off
Inertial Relief:	Off
Incompatible bonding options	Automatic
Large displacement	Off
Compute free body forces	On
Friction	Off
Use Adaptive Method:	Off
Result folder	SolidWorks document (C:\Users\149306\Desktop\Solidworks 2013\Oedometer Project\Fabrication folder for Oedometer)

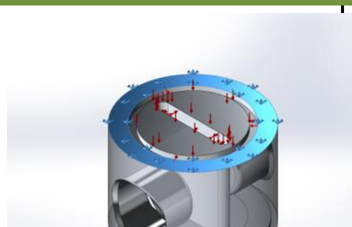
Units

Unit system:	SI (MKS)
Length/Displacement	mm
Temperature	Kelvin
Angular velocity	Rad/sec
Pressure/Stress	N/m^2

Material Properties

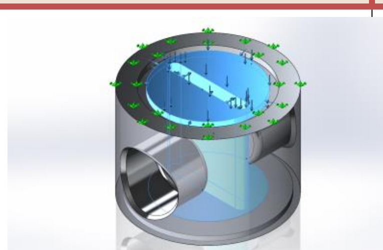
Model Reference	Properties	Components
	Name: **7075-T6 (SN)** Model type: **Linear Elastic Isotropic** Default failure criterion: **Max von Mises Stress** Yield strength: **5.05e+008 N/m^2** Tensile strength: **5.7e+008 N/m^2** Elastic modulus: **7.2e+010 N/m^2** Poisson's ratio: **0.33** Mass density: **2810 kg/m^3** Shear modulus: **2.69e+010 N/m^2** Thermal expansion coefficient: **2.36e-005 /Kelvin**	**SolidBody 1(Cut-Extrude11)(Oedometer sample holder)**
Curve Data:N/A		

Loads and Fixtures

Fixture name	Fixture Image	Fixture Details
Fixed-2		**Entities:** **1 face(s)** **Type:** **Fixed Geometry**

Resultant Forces

Components	**X**	**Y**	**Z**	**Resultant**
Reaction force(N)	**-23.1866**	**785.506**	**12.4389**	**785.946**
Reaction Moment(N-m)	**0**	**0**	**0**	**0**

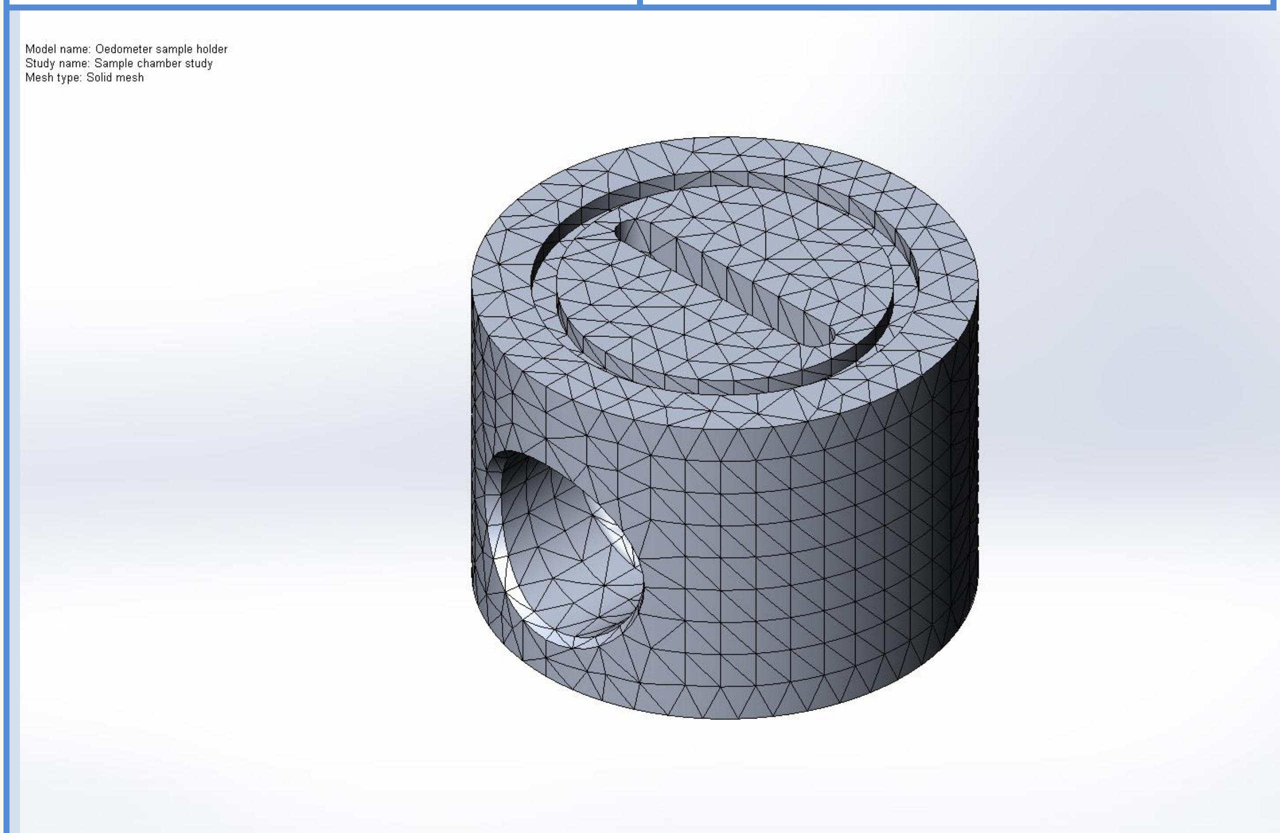
Load name	Load Image	Load Details
Pressure-1		**Entities:** **7 face(s)** **Type:** **Normal to selected face** **Value:** **4000** **Units:** **psi**

Mesh Information

Mesh type	Solid Mesh
Mesher Used:	Standard mesh
Automatic Transition:	Off
Include Mesh Auto Loops:	Off
Jacobian points	4 Points
Element Size	0.11072 in
Tolerance	0.00553601 in
Mesh Quality	High

Mesh Information - Details

Total Nodes	14266
Total Elements	8932
Maximum Aspect Ratio	4.8503
% of elements with Aspect Ratio < 3	99.2
% of elements with Aspect Ratio > 10	0
% of distorted elements(Jacobian)	0
Time to complete mesh(hh;mm;ss):	00:00:02
Computer name:	PN1288161



Resultant Forces

Reaction Forces

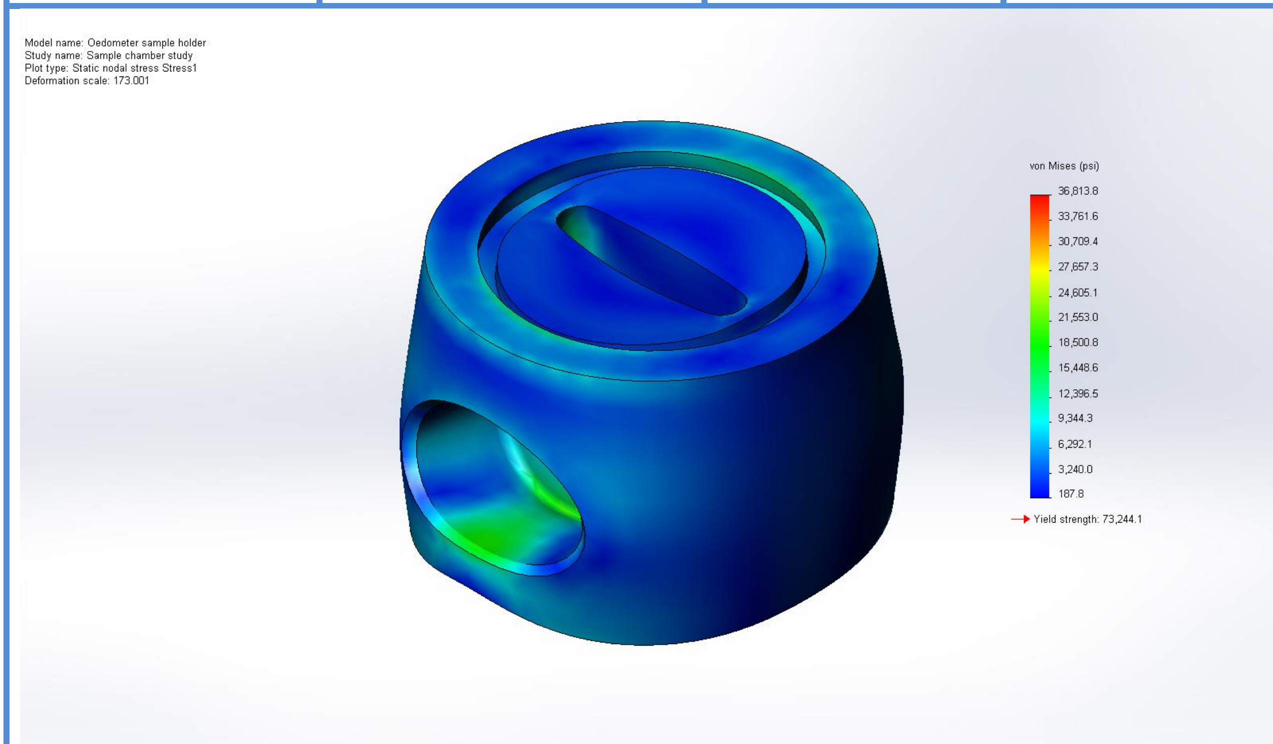
Selection set	Units	Sum X	Sum Y	Sum Z	Resultant
Entire Model	N	-23.1866	785.506	12.4389	785.946

Reaction Moments

Selection set	Units	Sum X	Sum Y	Sum Z	Resultant
Entire Model	N-m	0	0	0	0

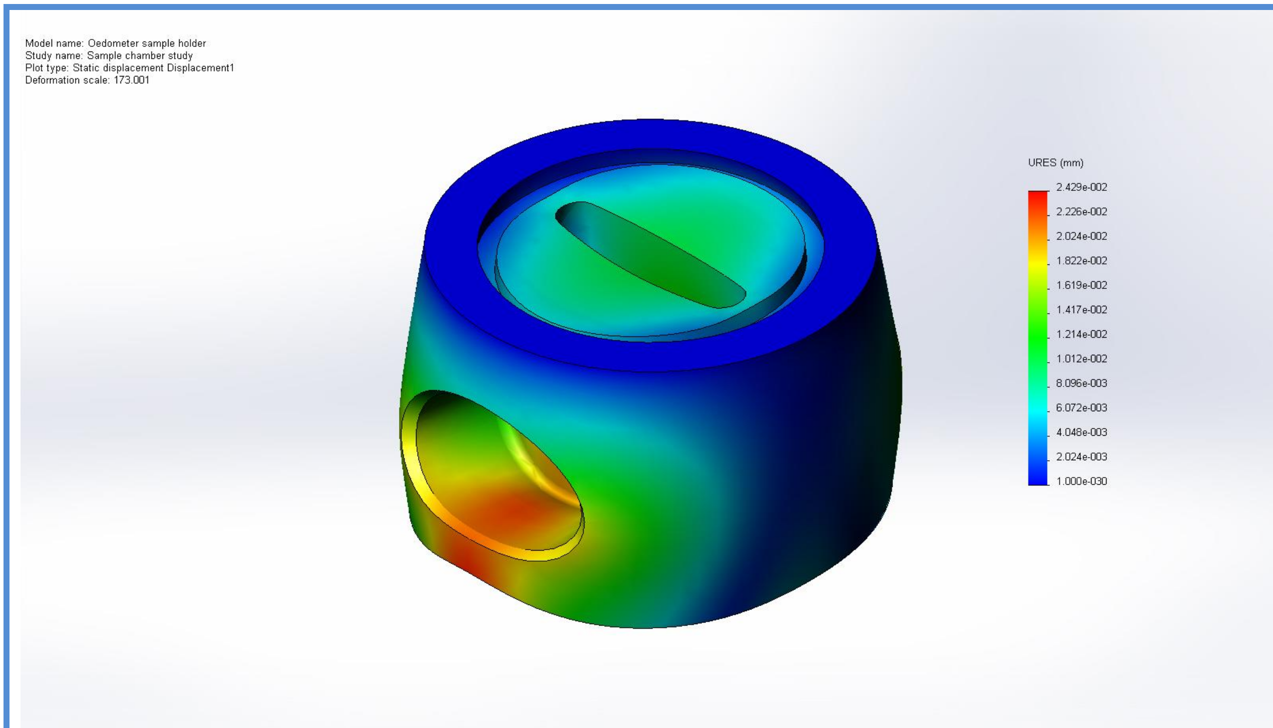
Study Results

Name	Type	Min	Max
Stress1	VON: von Mises Stress	187.815 psi Node: 777	36813.8 psi Node: 9887



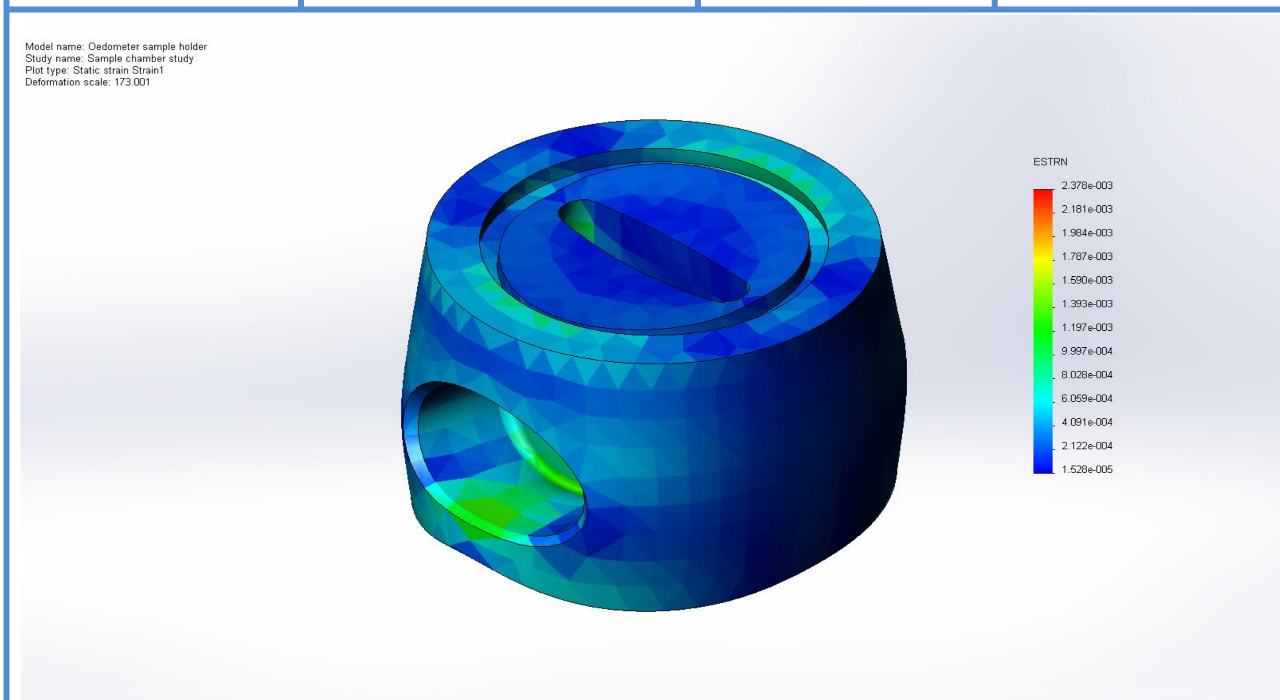
Oedometer sample holder-Sample chamber study-Stress-Stress1

Name	Type	Min	Max
Displacement1	URES: Resultant Displacement	0 mm Node: 221	0.0242887 mm Node: 13858



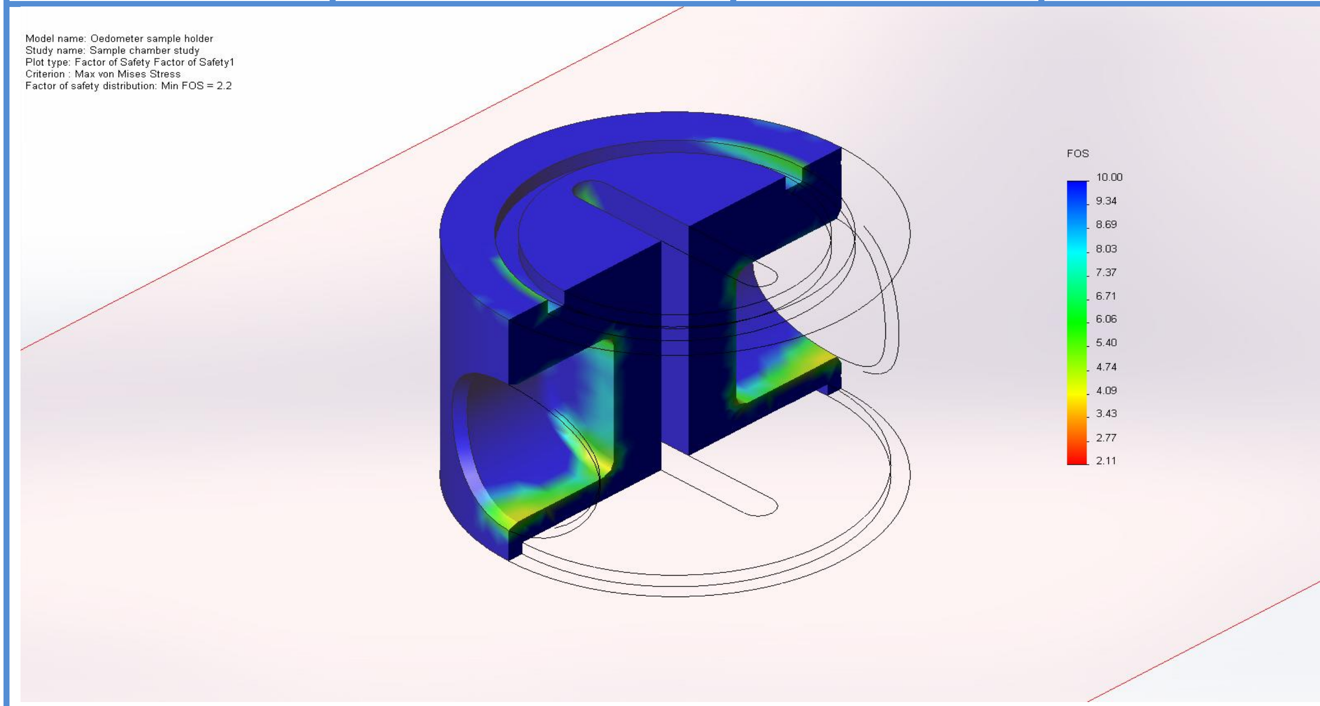
Oedometer sample holder-Sample chamber study-Displacement-Displacement1

Name	Type	Min	Max
Strain1	ESTRN: Equivalent Strain	1.52814e-005 Element: 3169	0.00237791 Element: 2665



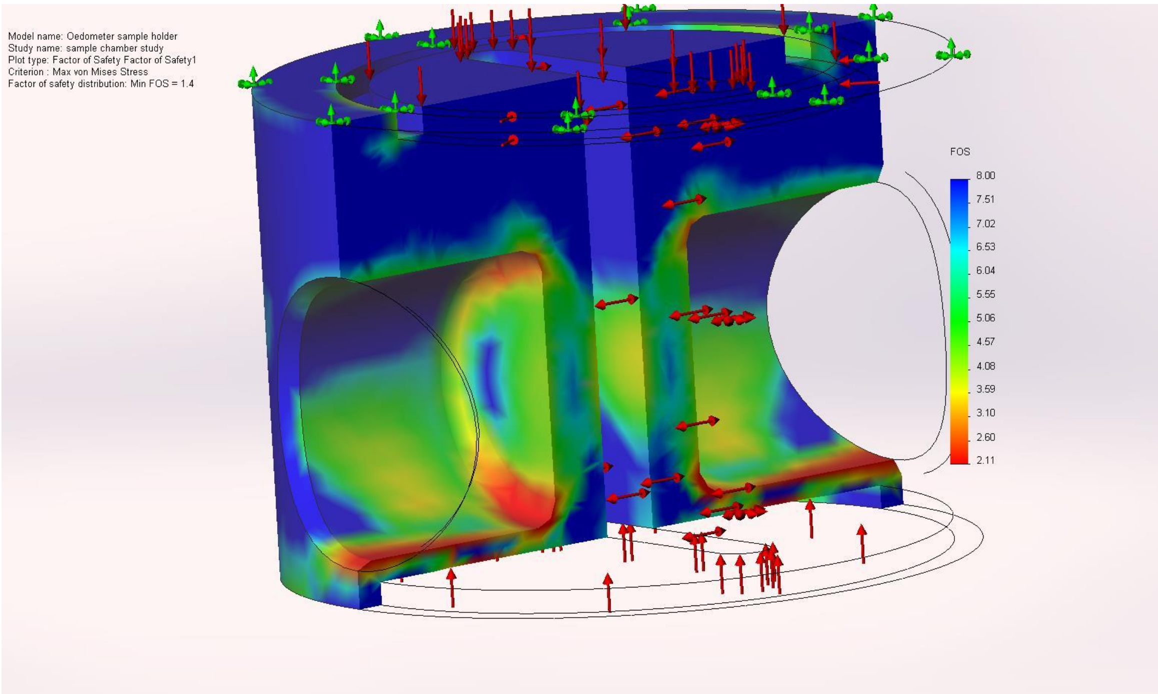
Oedometer sample holder-Sample chamber study-Strain-Strain1

Name	Type	Min	Max
Factor of Safety1	Max von Mises Stress	2.24567 Node: 9887	440.174 Node: 777

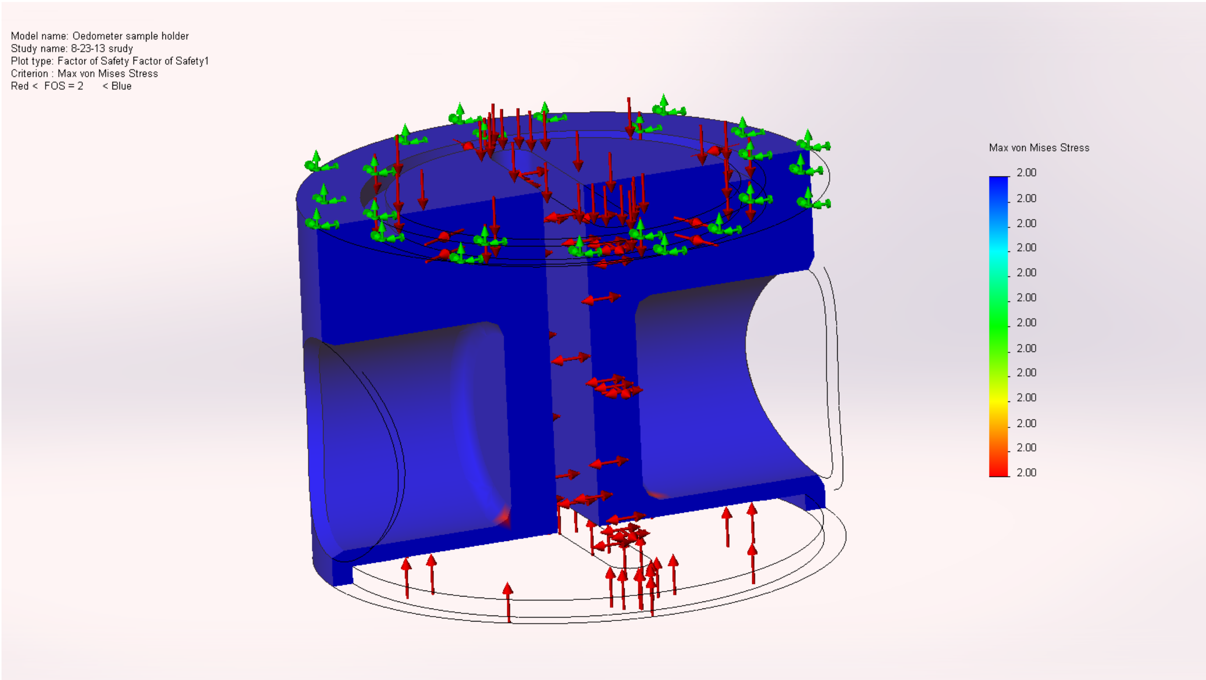


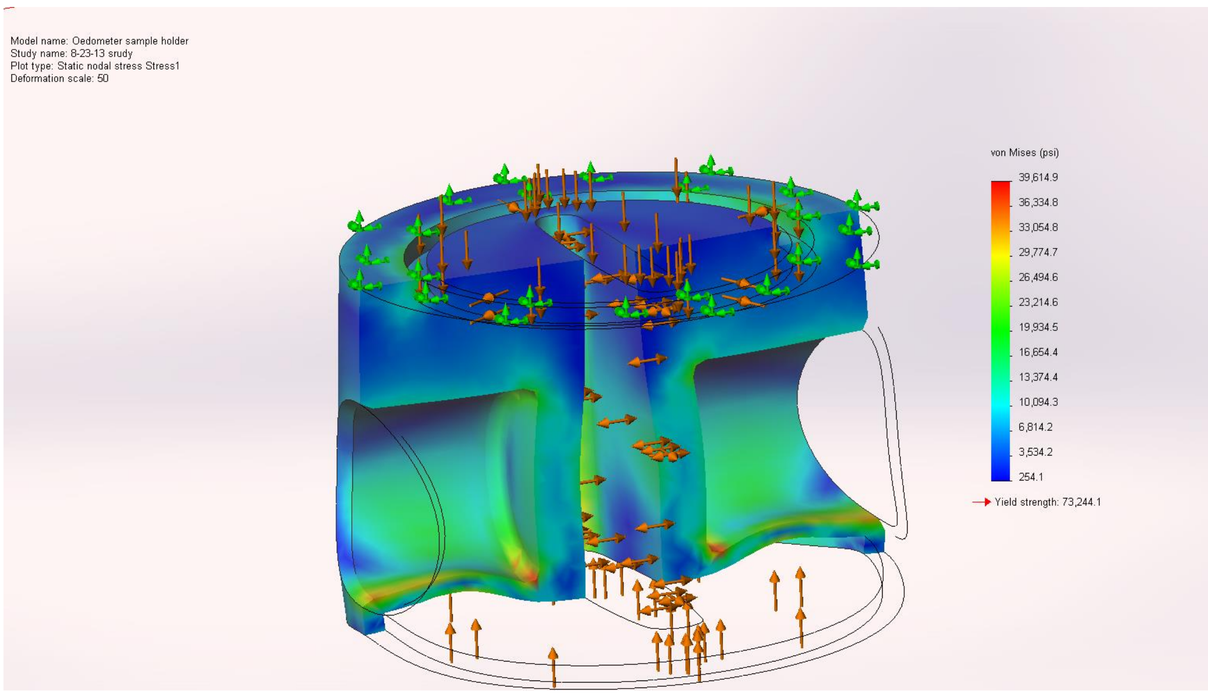
Oedometer sample holder-Sample chamber study-Factor of Safety-Factor of Safety1

The following figure is another view of the FOS. The figure contains the results of 5,200 psi, based on the yield strength of 7075 T6. The min FOS is shown on the left side of the figure legend with a value of 1.4.



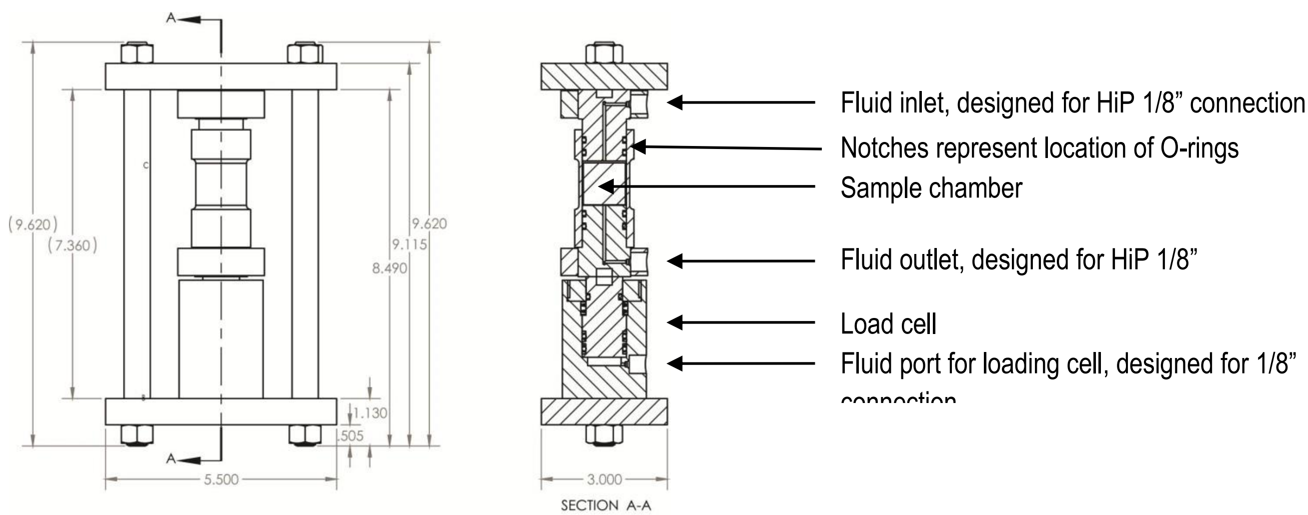
The following figure shows results using a finer mesh and is defined to show all places where the FOS is below 2. These areas should show in bright “red” based yield with a pressure of 4,000 psi. This means that according to the finite element analysis, there should have been no yielding until somewhere around 7,000 psi. According to the stress graph shown below the FOS graph, the maximum stress reached anywhere is 39,000psi, which is a little less than 3/5 of the yield strength.


Model name: Oedometer sample holder
Study name: 8-23-13 srudy
Plot type: Factor of Safety Factor of Safety1
Criterion : Max von Mises Stress
Red < FOS = 2 < Blue
Max von Mises Stress
2.00
2.00
2.00
2.00
2.00
2.00
2.00
2.00
2.00
2.00
2.00
2.00
2.00


Model name: Oedometer sample holder
Study name: 8-23-13 srudy
Plot type: Static nodal stress Stress1
Deformation scale: 50
von Mises (psi)
39,614.9
36,334.8
33,054.8
29,774.7
26,494.6
23,214.6
19,934.5
16,654.4
13,374.4
10,094.3
6,814.2
3,534.2
254.1
Yield strength: 73,244.1

S1.3. Design, Materials, and Finite Element Modeling of the Titanium Oedometer

The Titanium (Ti) oedometer contains a 1-inch (2.54 cm) diameter inner sample cavity for measuring “swelling” pressure as induced by clay samples subjected to dry or hydrous (i.e., water-bearing), sub- to supercritical CO_2. Figure S4 presents a schematic of the oedometer with annotation regarding fluid inlets and/or outlets, sample location, and dimensions. The maximum allowable working pressure (MAWP) of the entire oedometer system is 4000 psi (27.6 MPa).



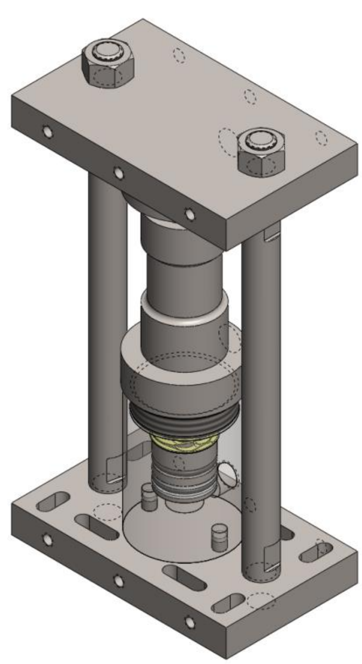


Figure S4. Schematic diagram of Ti oedometer (i.e., constant-volume pressure cell) with annotation indicated by arrows. Length dimensions are given in inches.

The oedometer is a custom-built design. The custom components include everything shown in the lower portion of Figure S4 (the 3D image), except for the o-rings and return spring within the load cell. The o-rings are composed of ethylene propylene and thus resistant to supercritical CO_2. The oedometer design is based on the following:

- All titanium construction (Ti 6Al-4V), for low neutron attenuation (for potential neutron applications)
- Piston retraction spring
- Pressure vessel safety factor of 4x

A thin-wall pressure vessel stress analysis was performed on the sample housing to estimate the factor of safety against yielding for the chamber. The plot of von Mises stress versus wall thickness is shown in Figure S5 and was derived from equations S2-S5. The plot shows that with an ID of 1.05 in, an outer diameter of 1.21 in (0.079 in wall) provides a factor of safety of 4x against yielding.

$$\sigma_t = \frac{Pi*ri^2*\left(1+\frac{ro^2}{ri^2}\right)}{(ro^2-ri^2)} \tag{S2}$$

$$\sigma_r = \frac{Pi*ri^2}{(ro^2-ri^2)}*\left(1-\frac{ro^2}{ri^2}\right) \tag{S3}$$

$$\sigma_z = 0 \tag{S4}$$

$$\sigma_{vm} = \sqrt{\frac{(\sigma_t - \sigma_r)^2 + (\sigma_r - \sigma_z)^2 + (\sigma_z - \sigma_t)^2}{2}} \quad \text{(S5)}$$

where σ_t is the tangential stress, σ_r is the radial stress, σ_z is the axial stress and σ_{vm} is the von Mises stress. Pi, r_i, and r_o are the internal pressure, pressure vessel inside radius, and pressure vessel outside radius respectively.

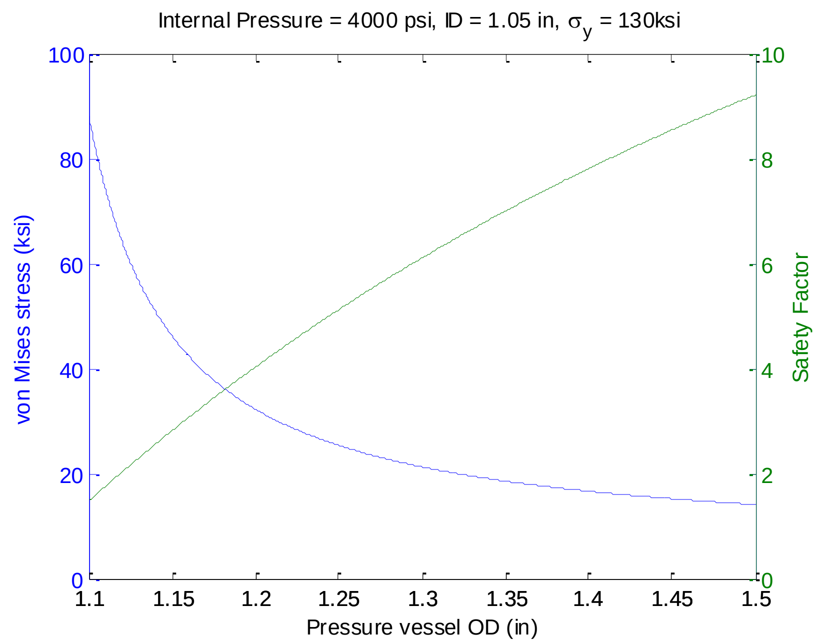


Figure S5. Result of thin-wall pressure vessel analysis to determine factor of safety for the sample chamber wall thickness.

A FEM analysis was performed on the actual part as a confirmation of the thin-wall analysis (Figure S6). The results of that simulation are shown below. For an internal pressure of 4000 psi, the von Mises stress in the housing is approximately 30 ksi. This is consistent with the thin-wall assumption for the previous analysis. The FEM results also show a factor of safety against yielding of 4x.

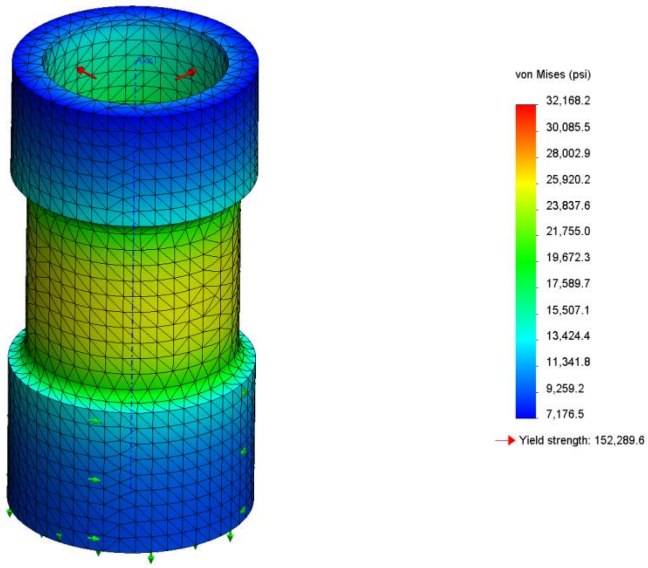


Figure S6. FEM analysis to determine factor of safety for the sample chamber wall thickness.

For the load cell portion of the oedometer, FEM was used to estimate the stresses in the body for a 4000 psi internal pressure. The results shown in Figure S7 indicate that there is substantial margin against yielding for the load cell portion of the vessel. Assuming a yield strength of 130 ksi, the factor of safety against yielding for the load cell housing is approximately 15x.

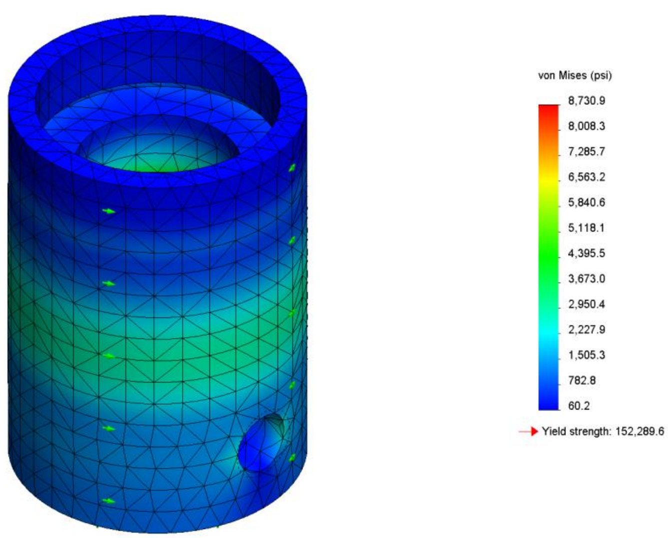


Figure S7. FEM analysis to determine factor of safety for the load cell.

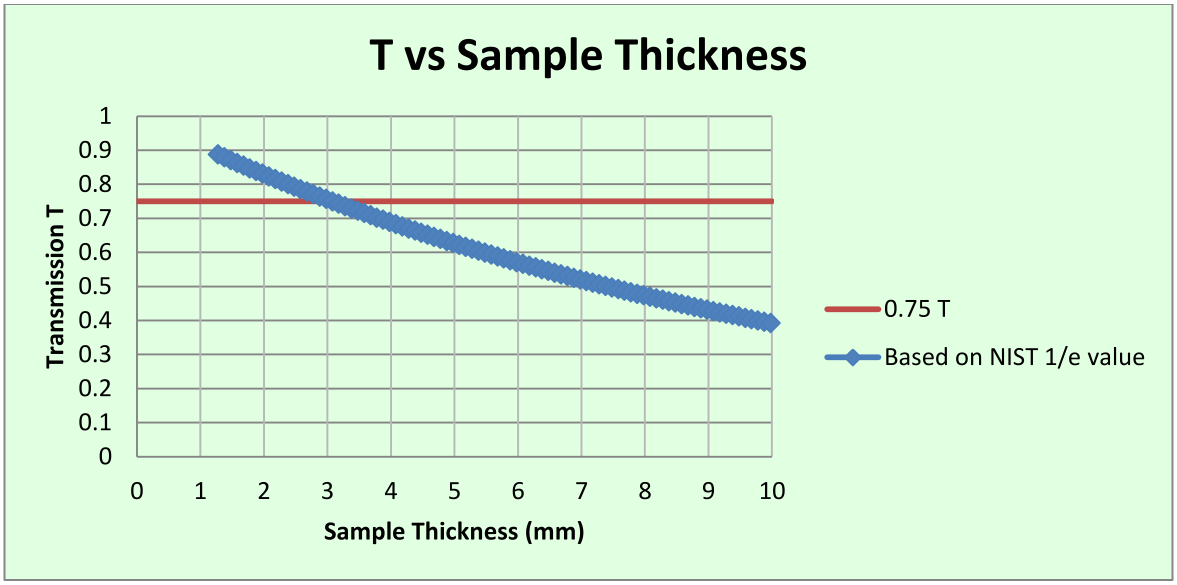
Overpressure testing to 1.3 x MAWP (i.e., 5300 psi) was performed by filling the vessel sample chamber with water, plugging the ports and applying a pressure gradient to the peak pressure through the load cell housing. The fluid medium used to pressurize the load cell housing was Isopar H fluid. Once the fluid reached 5300 psi, it was held at constant pressure for seven hours to determine if leaks were present and measure any strain through strain gages mounted on the outside of the vessel within the gauge length. Two identifical Ti oedometer vessels were built. One vessel is designated as Oedometer-Ti-A and Oedometer-Ti-B. Both vessels were tested using this procedure.

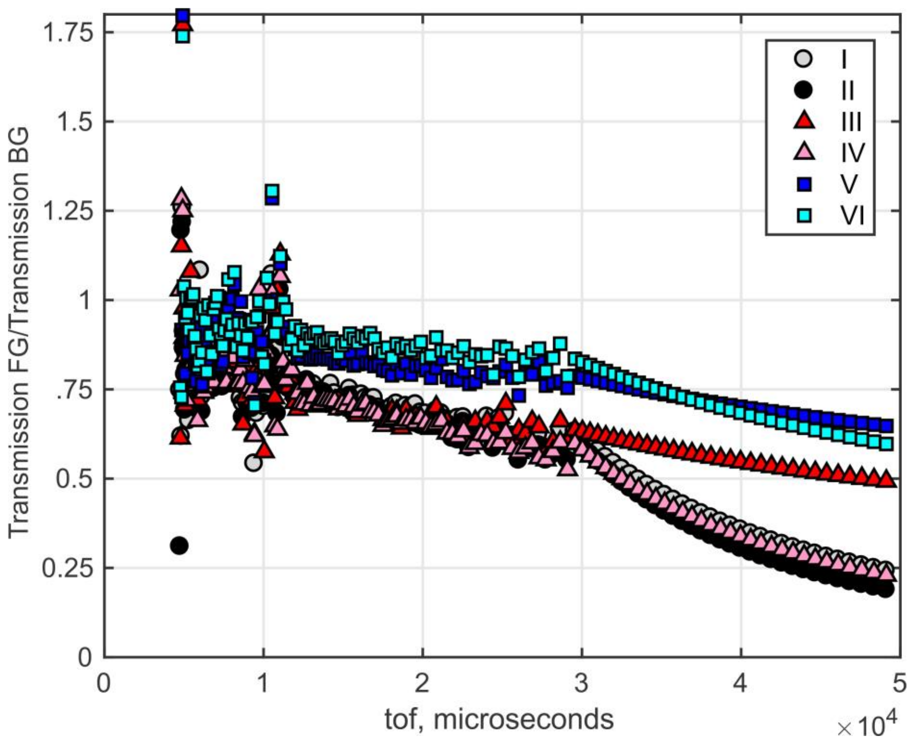
S2. Neutron Beam Transmission as a Function of Sample Thickness, and Assessment of Multiple Scattering and Anisotropy

Calculations of neutron beam transmission through SWy-2 bentonite were performed using information from the NIST scattering length density online calculator at: https://www.ncnr.nist.gov/resources/sldcalc.html. Transmission > 0.75 is sought to avoid multiple scattering. The compound name used in the calculator was the following, as only integer stoichiometry is supported in the calculator: Ca12Na32K5Al303Fe41Mn1Mg54Ti2Si798Al2O2400H400. For the calculation, we assume pure smectite with no pore space. The NIST calculator provided scattering length density and neutron 1/e values, which were used in the following equation and to generate Figure S1:

$$T = \frac{I(d)}{I_0} = e^{-\Sigma_T d} \qquad \text{(S1)}$$

A thickness of 3.08 mm corresponds to a transmission of 0.75 (Figure S1).


T vs Sample Thickness
Transmission T
Sample Thickness (mm)
0.75 T
Based on NIST 1/e value
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0 1 2 3 4 5 6 7 8 9 10


Transmission FG/Transmission BG
tof, microseconds
×10^4
I
II
III
IV
V
VI
1.75
1.5
1.25
1
.75
0.5
0.25
0
0 1 2 3 4 5

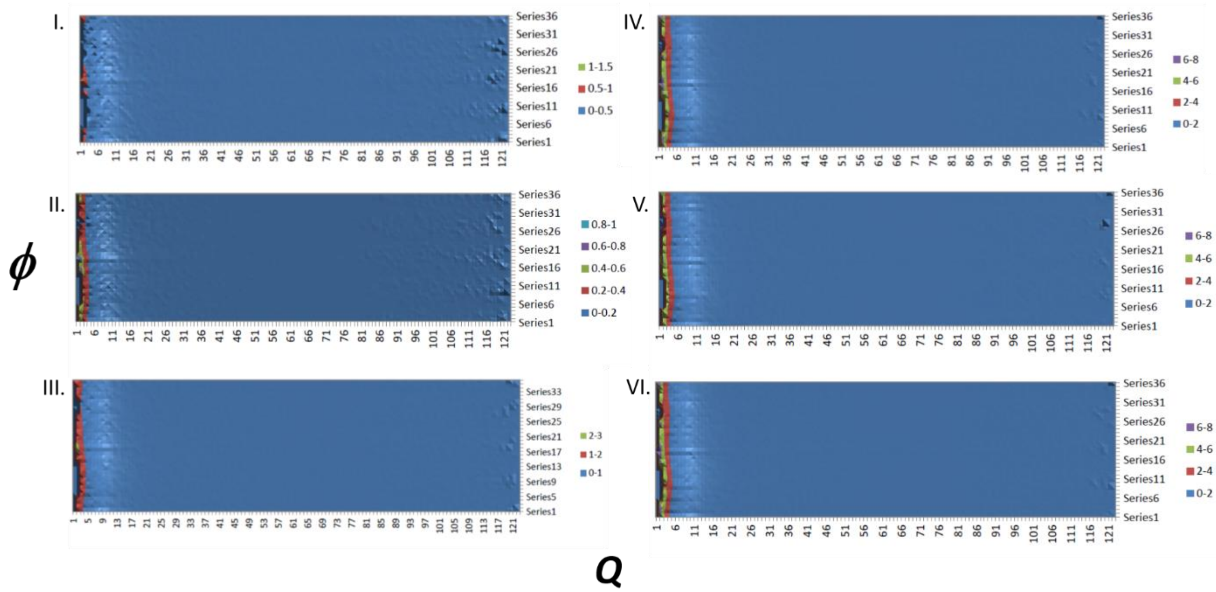


Figure S8. (Top) Neutron transmission versus sample thickness for SWy-2 bentonite. **(Middle)** Transmission of neutron beam through samples normalized by transmissions through the empty sample chamber versus time of flight (tof). Legend corresponds to Roman numerals of Section 3.2. (**Bottom**) Assessment of anisotropy in Q from assessment of Q variation as a function of azimuth, ϕ. The lack of any cusps or horizontal "streaks" in Q suggest there is little anisotropy in the scattering vector response for all loading conditions in our Oedometric SANS experiments. Here we show raw pixel data and not derived Q values. Legend corresponds to Roman numerals of Section 3.2.

The greatest amounts of multiple scattering occur in the less consolidated sample measurements, and the dry CO_2 measurement at zero effective stress (Figure S8 in Supporting Information). Consolidation to higher effective stresses and wet pore conditions comparatively decreases multiple scattering.

S3. SANS Interpretation and Parameter Sensitivity

Screenshots and information on the use of the Pore Size Distribution macros of the Irena package version 2.61 (Ilavsky and Jemian, 2009) with Igor Pro version 6.37 are given here. These screenshots are provided so that the reader can know exactly what parameters were chosen, and how the derivation of void distributions were done. These data are presented following the experimental stages as in main text (Section 3.1).

S3.1. Stage I Dry Consolidation

Stage I is compression of the bentonite clay in the sample chamber at a mass of 1.7 g and initial volume of 1.7206 cm^3 under ~5 psig axial load on the hydraulic piston (or 7.74*5 psig to obtain the load on the clay itself). The Unified Fit model requires one level only. The pore filling fluid is assumed to be at 1 atm (14.67 psia) and 100% nitrogen to represent air. Scattering length densities and contrast for the clay and nitrogen is given in Table 1 in the main text. Figure S9 presents the Unified Fit parameters and results. Figure S10 presents the pore size distribution. Note that to obtain fits, the errors are multiplied by a value less than 1. For comparison, a scattering contrast between clay and vacuum ($10.753 *10^{20}$ cm^{-4}) results in a relative change for the size volume distribution from the clay-N_2 case by ~0.5% or less. The choice of the final point at higher Q while fitting the data can affect the pore size distribution of the smallest scatterers. For example, choosing point 70 versus point 75 results in a shift of the peak to the smaller pore diameters with a higher peak, but the overall shape of the curve is not changed (Figure 12). As the choice of the final point in the fitting at higher Q can strongly affect the estimation of the smaller pores of the pore size distributions, we choose to fit each curve to the point 70 to have a consistent comparison. Some of the data at higher Q than point 70 may be real, but these will be neglected to achieve consistency of analysis from the different stages of the experiment (see Section 3.1 in the main text).

S3.2. Stage II Dry Consolidation

Stage II is compression is ~39 psig axial load on the hydraulic piston (or 7.74*39 psig to obtain the load on the clay itself). The Unified Fit model requires one level only. The pore filling fluid is assumed to be 100% nitrogen to represent air and at 1 atm (14.67 psia). The scattering length densities and scattering contrast for the clay and nitrogen is given in Table 1. Figure S13 presents the Unified Fit parameters and results. Figure S14 presents the pore size distribution. For comparison, a scattering contrast between clay and vacuum ($10.753 * 10^{20}$ cm^{-4}) results in relative differences for the size volume distribution from the clay-N_2 case by ~0.4% or less. Based on the strain of the titanium oedometer experiment, the aspect ratio of an oblate of 1.144 may represent the shape of the pores better than a sphere. Figure 15 plots the spherical versus oblate spheroid (at 1.144 aspect ratio) pore volume distributions for Stage II, illustrating that the two curves are very similar.

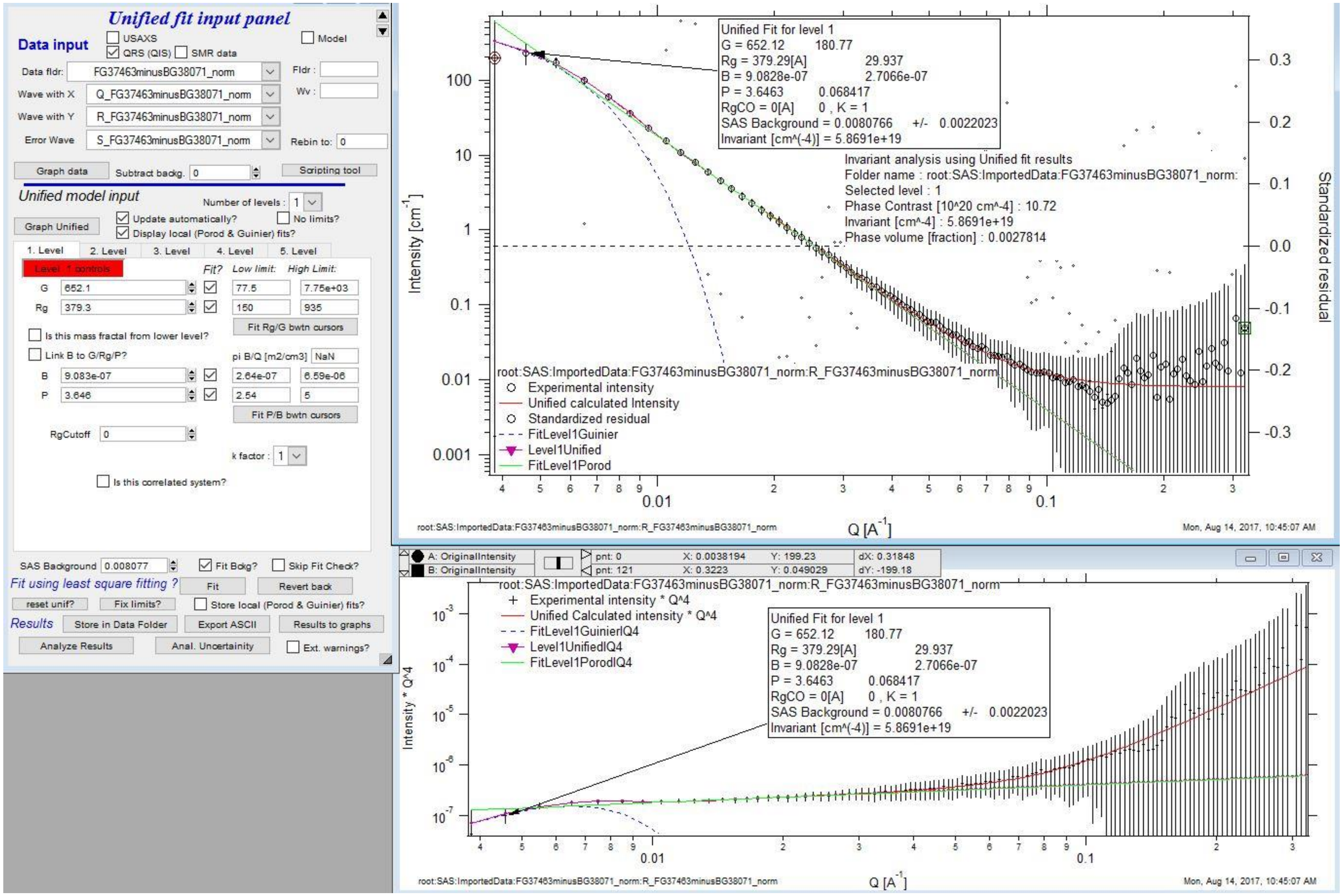


Figure S9. Screenshot of Unified Fit parameters and results for Stage I (sample ID 37463). Note that the correct scattering contrast was used in the fitting.

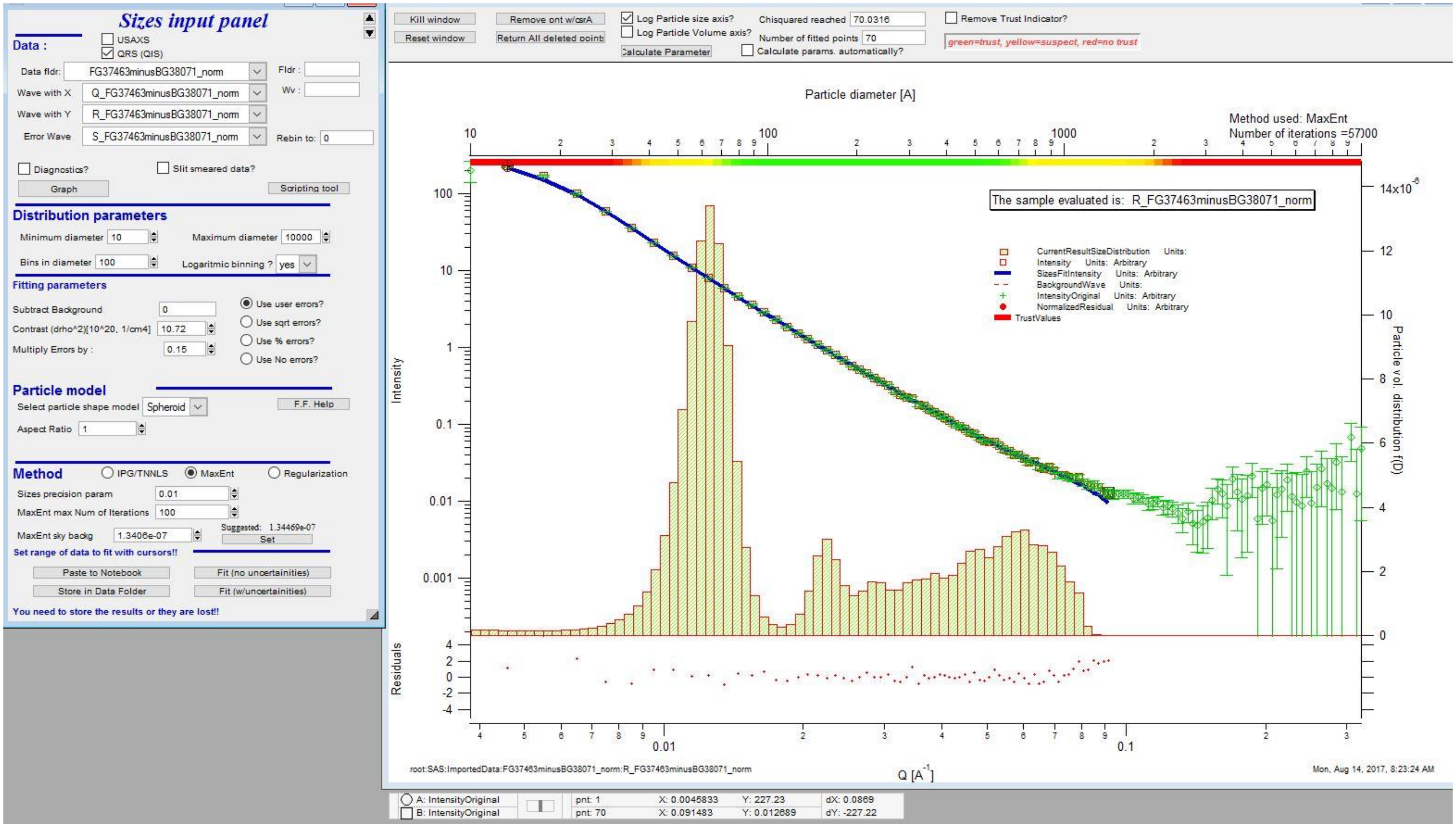


Figure S10. Screenshot of Pore Size Distribution parameters and results for Stage I (sample ID 37463).

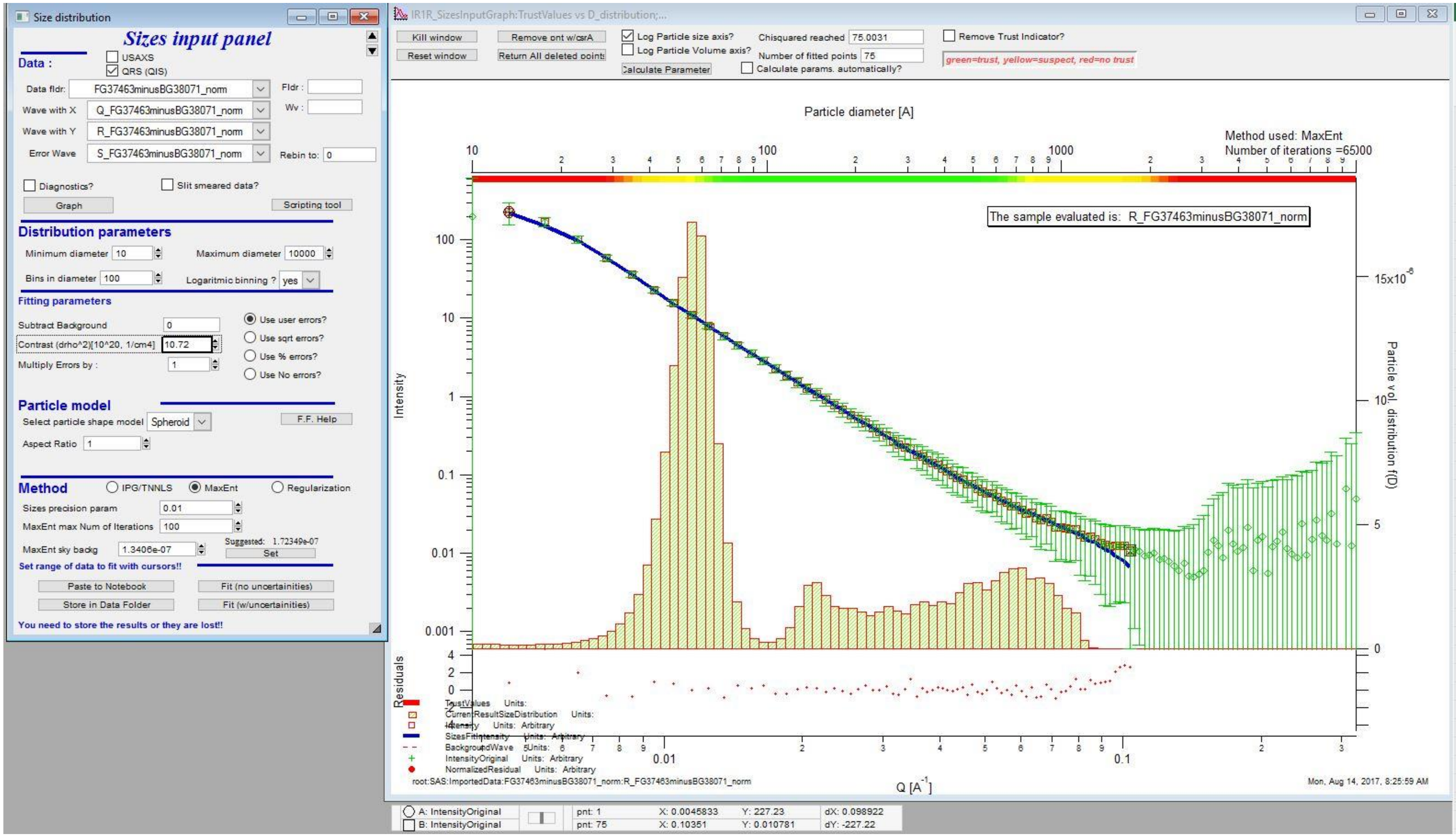


Figure S11. Screenshot of Pore Size Distribution paramters of Figure S10, but fit to point 75 (not point 70). Also, the "Multiply Errors by" is set to one to show the plotting of the full error bars (although the value of 0.15 was used in fitting the data).

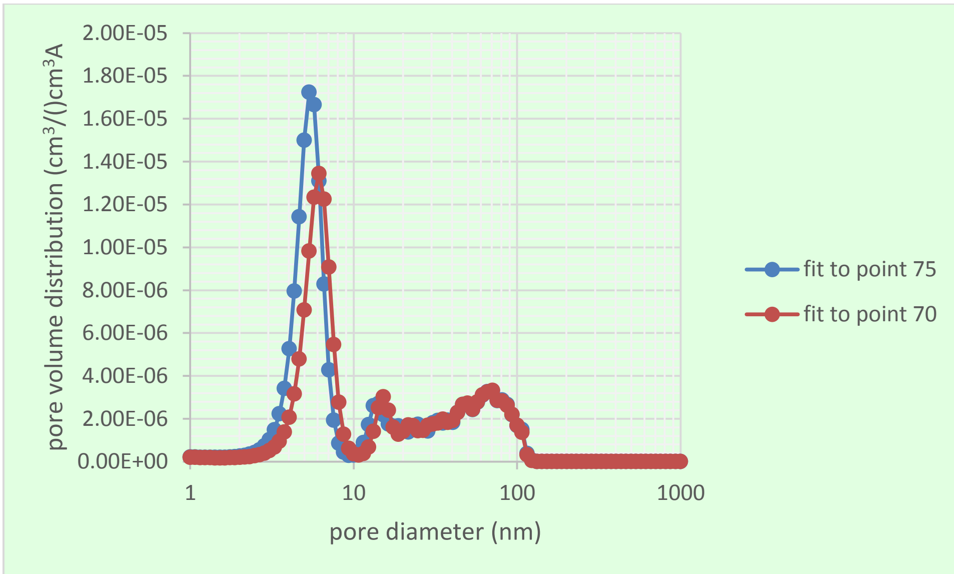


Figure S12. Pore volume distributions for the data set of Stage I, with curves fit to point 70 and point 75.

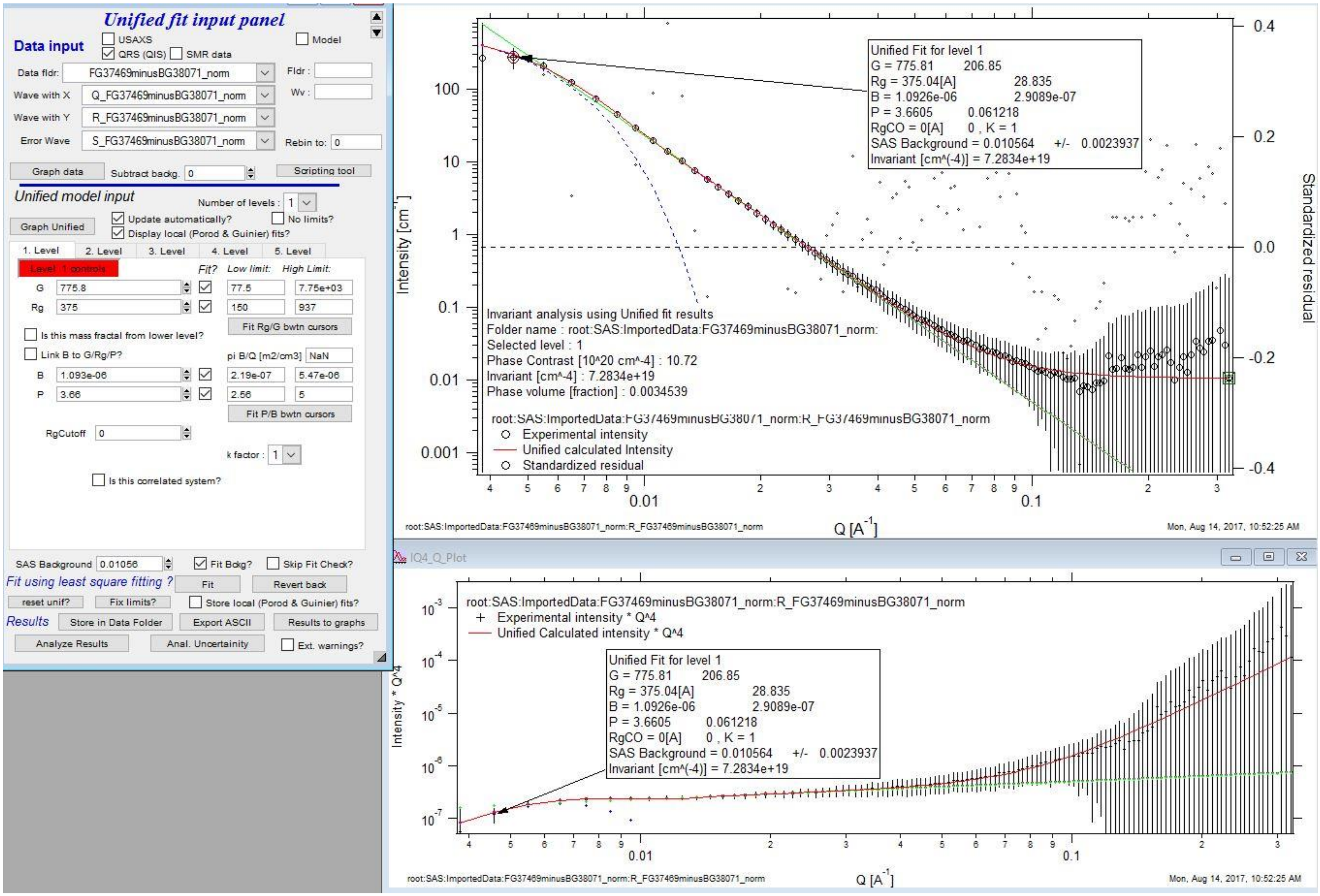


Figure S13. Screenshot of Unified Fit parameters and results for Stage II (sample ID 37469).

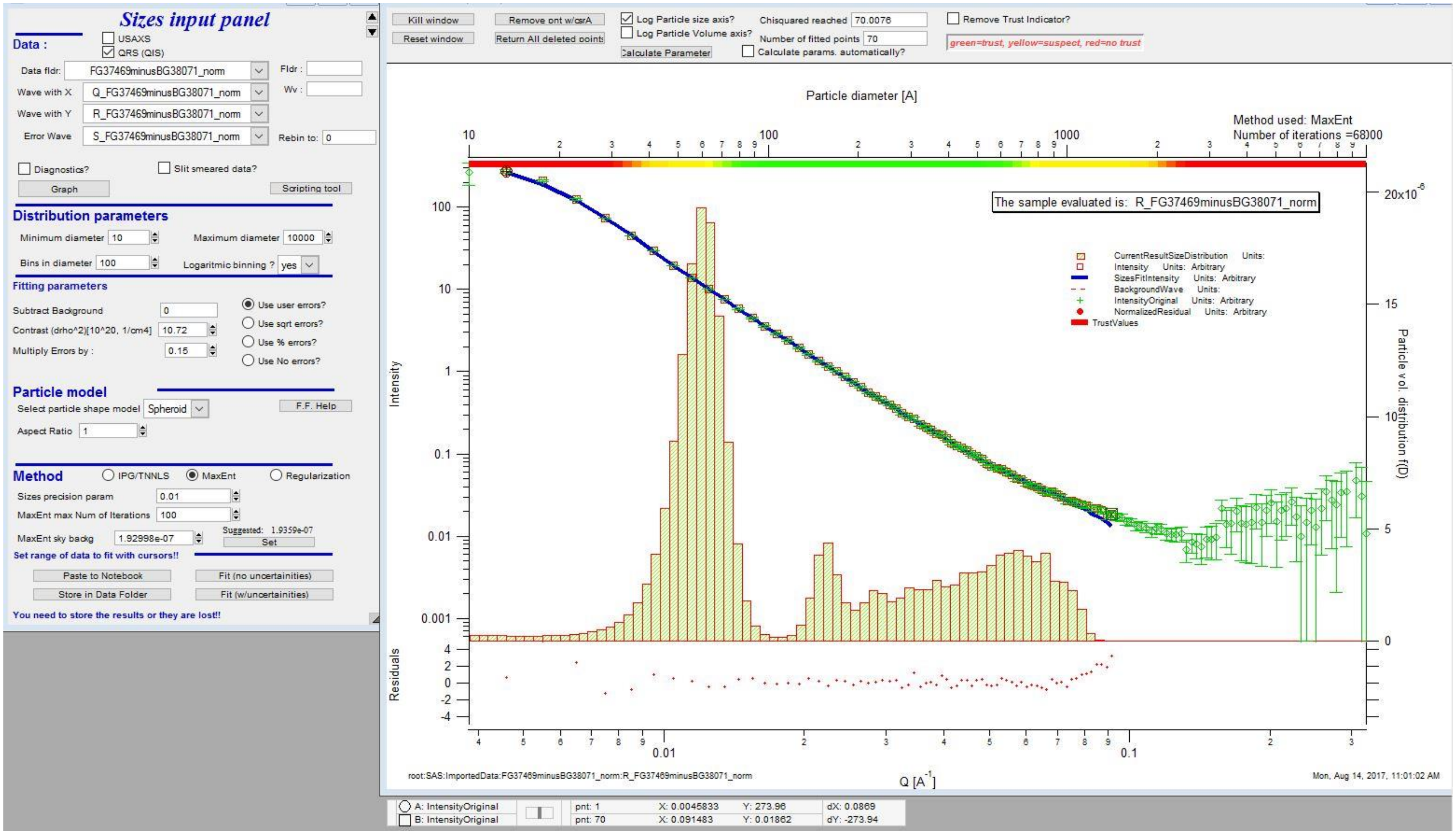


Figure S14. Screenshot of Pore Size Distribution parameters and results for Stage II (sample ID 37469), fit to point 70.

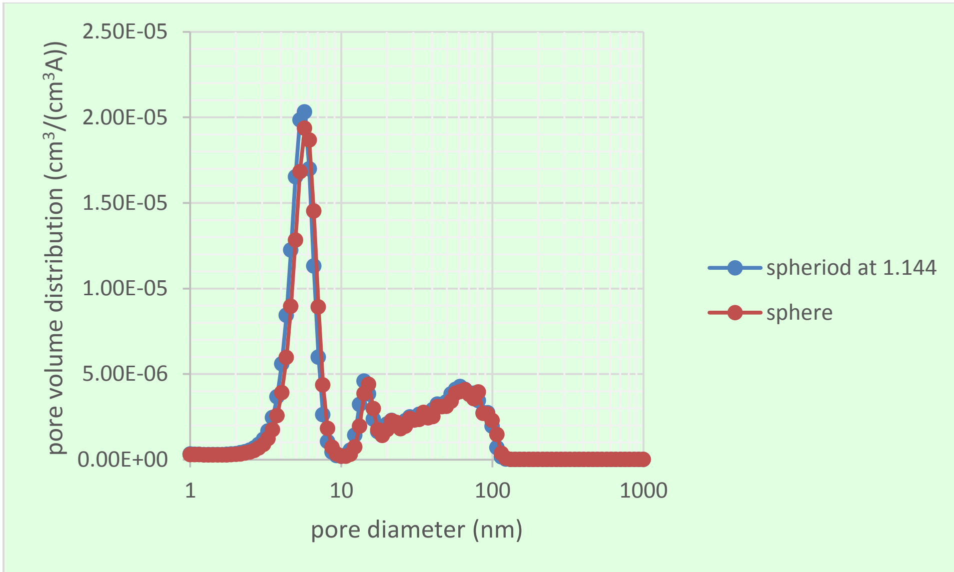


Figure S15. Pore volume distribution for Stage II modeled with spherical pore shapes versus oblate spheroid pore shapes at 1.144 aspect ratio.

S3.3. Stage III Hydrostatic Pressurization with Dry CO_2

Stage III compression is with dry CO_2 at pore pressure of approximately ~930 psig. Assuming dry pure CO_2 at a density of 0.817 g/cm^3 (at a temperature of 18°C), the scattering contrast with the bentonite clay is 1.535 10^{20} cm^{-4}. Figure S16 presents the Unified Fit results. Figure S17 gives the pore volume distribution for Stage III. Figure S18 illustrates that the sphere versus spheroid at aspect ratio of 1.123 pore shape (as based on the titanium experiment and the amount of strain) results in little change to the pore size distribution.

S3.4. Stage IV Post-Dry CO_2 Consolidation

Stage IV compression decreases the pore pressure to approximately 1 atm or ~ 0 psig (assuming 14.70 psia). The valve was closed after depressurizing to kept any sorbed or free CO_2 in the sample and from exchanging with atmospheric gases. Assuming dry pure CO_2 at a density of 1.85 g/cm^3 (at a temperature of 18°C), the scattering contrast with the bentonite clay is

1.535×10^{20} cm^{-4}. Figure S19 presents the Unified Fit model results. Figure S20 gives the pore volume distribution for Stage III. Figure S21 illustrates that the sphere versus spheroid at aspect ratio of 1.202 pore shape (as based on the titanium experiment and the amount of strain) results in little change to the pore size distribution.

S3.5. Stage V Hydrostatic Pressurization with Wet CO_2

Stage V involved increasing the pore pressure to approximately 836 psig with wet CO_2; that is, CO_2 saturated with D_2O. The mass fraction of water (H_2O) dissolved in CO_2 at 836 psi is 0.001049 (Y_{H2Og}; see Section S.4.8). We assume that the dissolution of D_2O in CO_2 is similar to H_2O dissolved in CO_2—at the time of these calculations, we do not have an estimate of D_2O dissolution in CO_2. We use the Scattering Contrast tool in Irena to obtain the scattering contrast of water-saturated CO_2. The Scattering Contrast tool inputs integer values of stoichiometric coefficients; thus, the formula we use to represent Y_{H2Og} at 0.001049 in the tool is C998951O1997902D2098O1049. The scattering contrast of the wet CO_2 and the SWy-2 clay is 1.635×10^{20} cm^{-4}, which assumes a density of 800.81 kg/m^3 (at a temperature of 18°C and a pressure of 836 psi—see Section S.4.8). Figure S22 presents the Unified Fit model parameters and results. Figure S23 gives the pore volume distribution for Stage V. Figure S24 illustrates that the sphere versus spheroid at aspect ratio of 1.207 pore shape (as based on the titanium experiment and the amount of strain) results in little change to the pore size distribution.

S3.6. Stage VI Post-Wet CO_2 Consolidation

Stage VI is the change from high pressure wet CO_2 to low pressure wet CO_2 by opening the port to the pore fluid and allowing it to depressurize. After depressurization, the valve was closed to keep atmospheric gases from exchanging with possibly sorbed CO_2 and water or the wet CO_2 in the pores. The pore pressure when placed in the beam was approximately 3 psig. Using approximately atmospheric pressure (14.7 psia), the density of wet CO_2 of 0.18531 kg/m^3, and the mass fraction of 0.0084921 of H_2O in CO_2 at 18°C (see Section S.4.8), we obtain a scattering contrast of 10.72×10^{20} cm^{-4} using the Scattering Contrast tool of Irena. The Scattering Contrast tool inputs integer values of stoichiometric coefficients; thus, the formula we use to represent Y_{H2Og} at 0.0084921 in the tool is C9915079O19830158D169842O84921. Figure S25 presents the Unified Fit model parameters and results. Figure S26 gives the pore volume distribution for Stage VI. Figure S27 presents the pore size distribution as based on the sphere versus spheroid at aspect ratio of 1.461 pore shape (as based on the titanium experiment and the amount of strain). The pore size distribution results have the greatest change for sphere versus spheroid as compared to the other experiments stages.

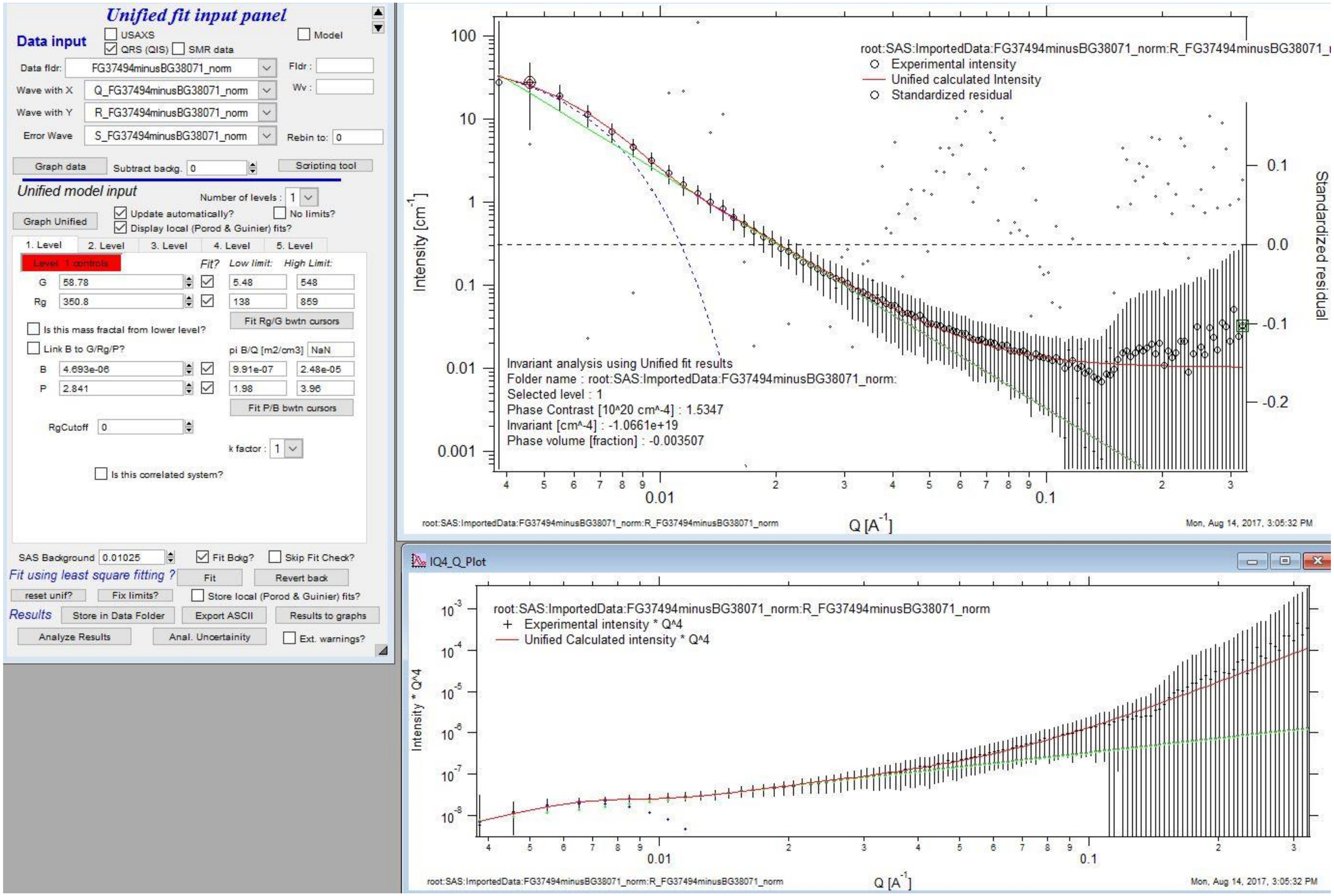


Figure S16. Screenshot of Unified Fit parameters and results for Stage III (sample ID 37494).

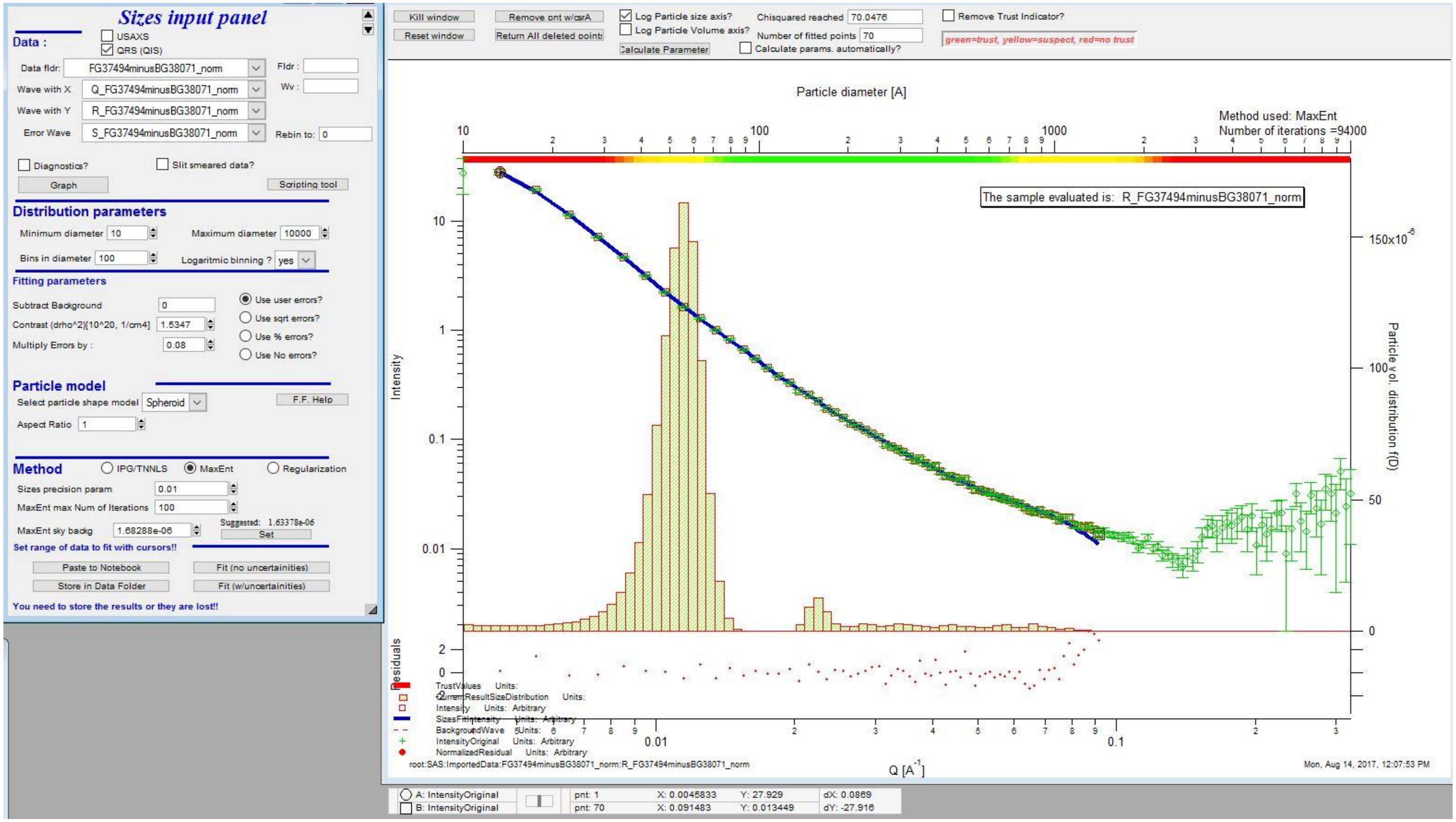


Figure S17. Screenshot of Pore Size Distribution parameters and results for Stage III (sample ID 37494), fit to point 70.

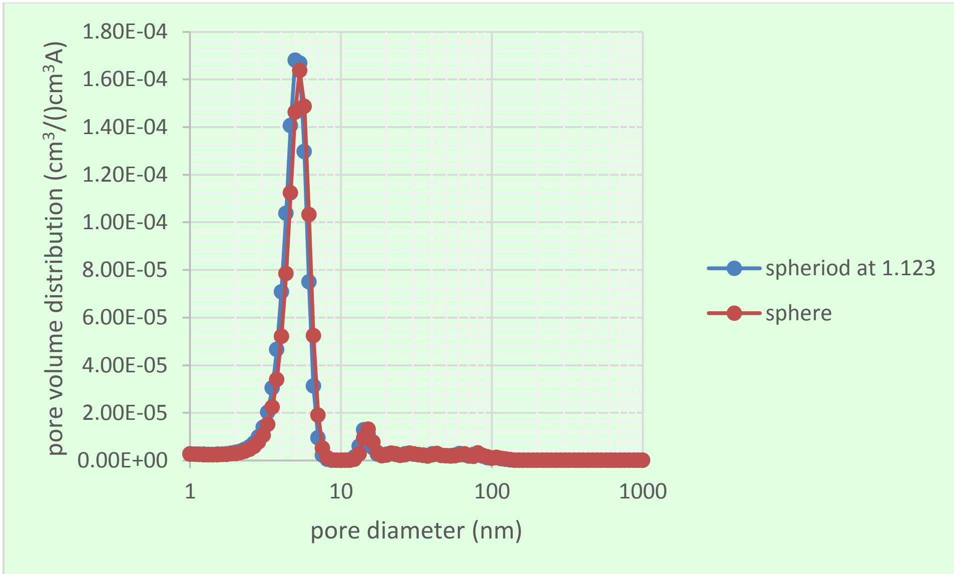


Figure S18. Pore volume distribution for Stage III modeled with spherical pore shapes versus oblate spheroid pore shapes at 1.123 aspect ratio.

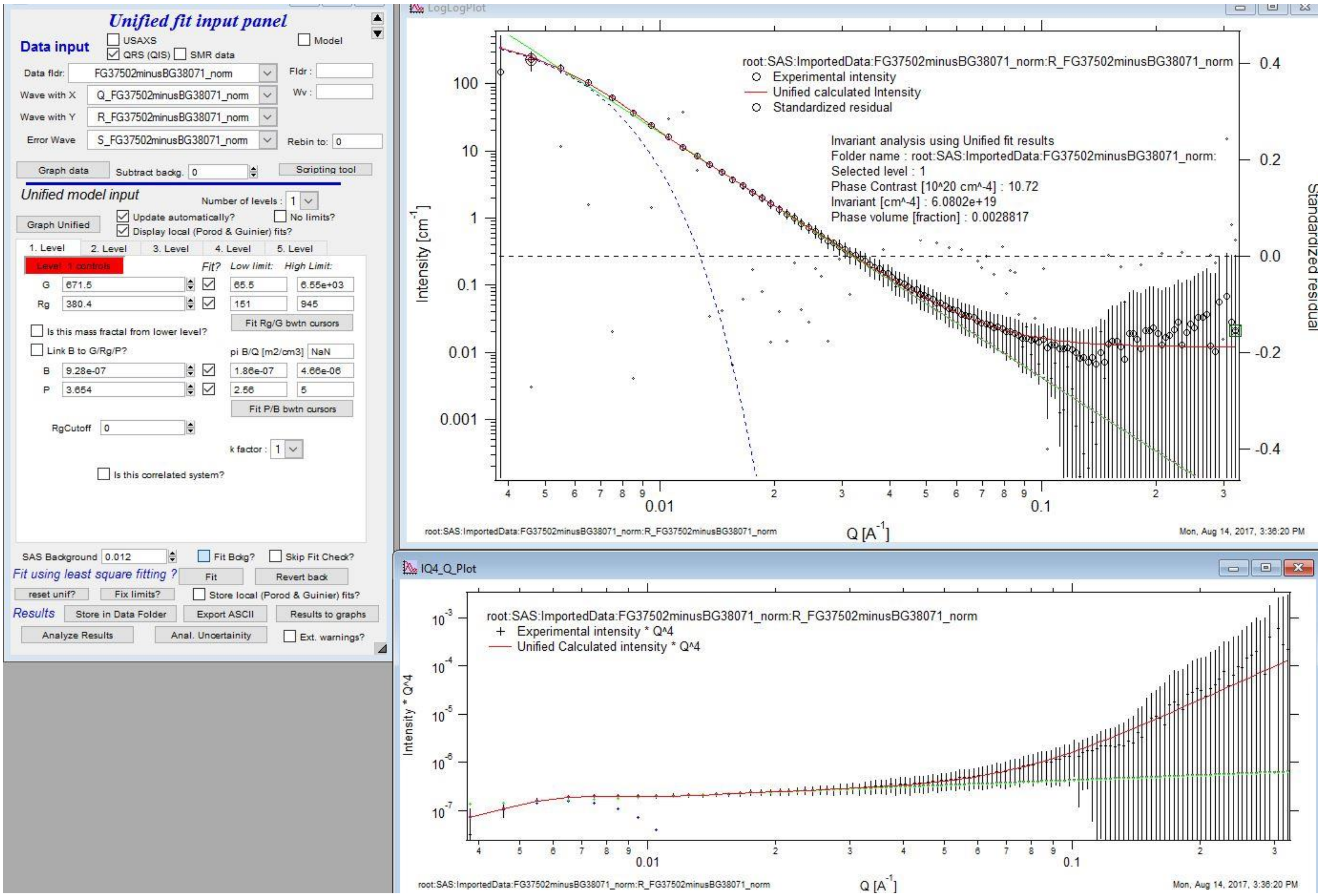


Figure S19. Screenshot of Unified Fit parameters and results for Stage IV (sample ID 37502).

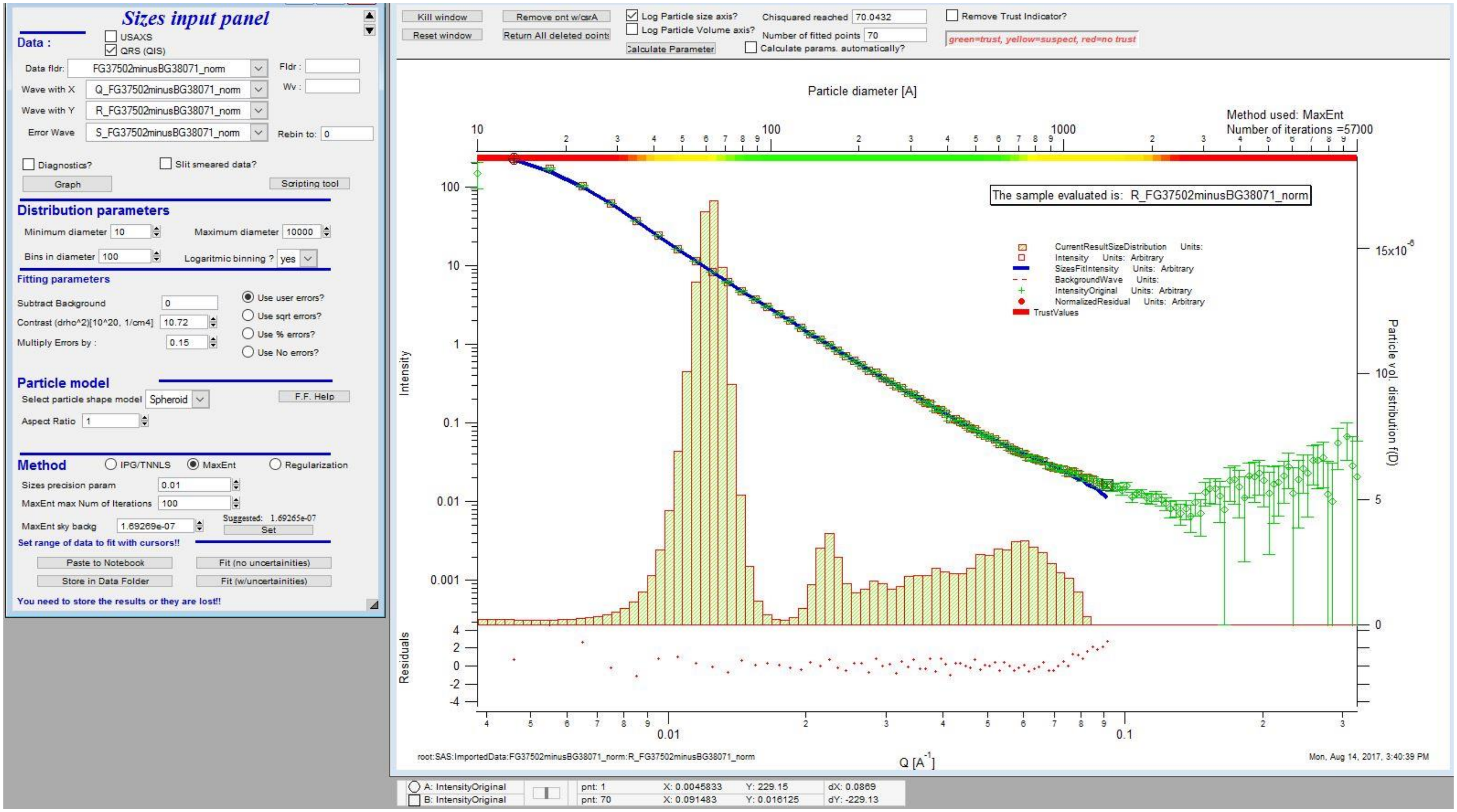


Figure S20. Screenshot of Pore Size Distribution parameters and results for Stage IV (sample ID 37502), fit to point 70.

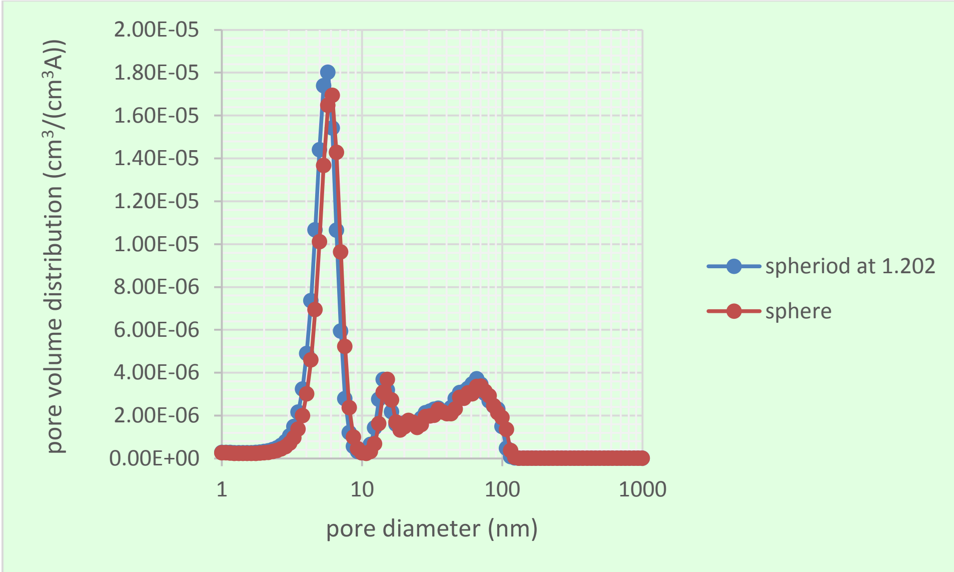


Figure S21. Pore volume distribution for Stage IV modeled with spherical pore shapes versus oblate spheroid pore shapes at 1.202 aspect ratio.

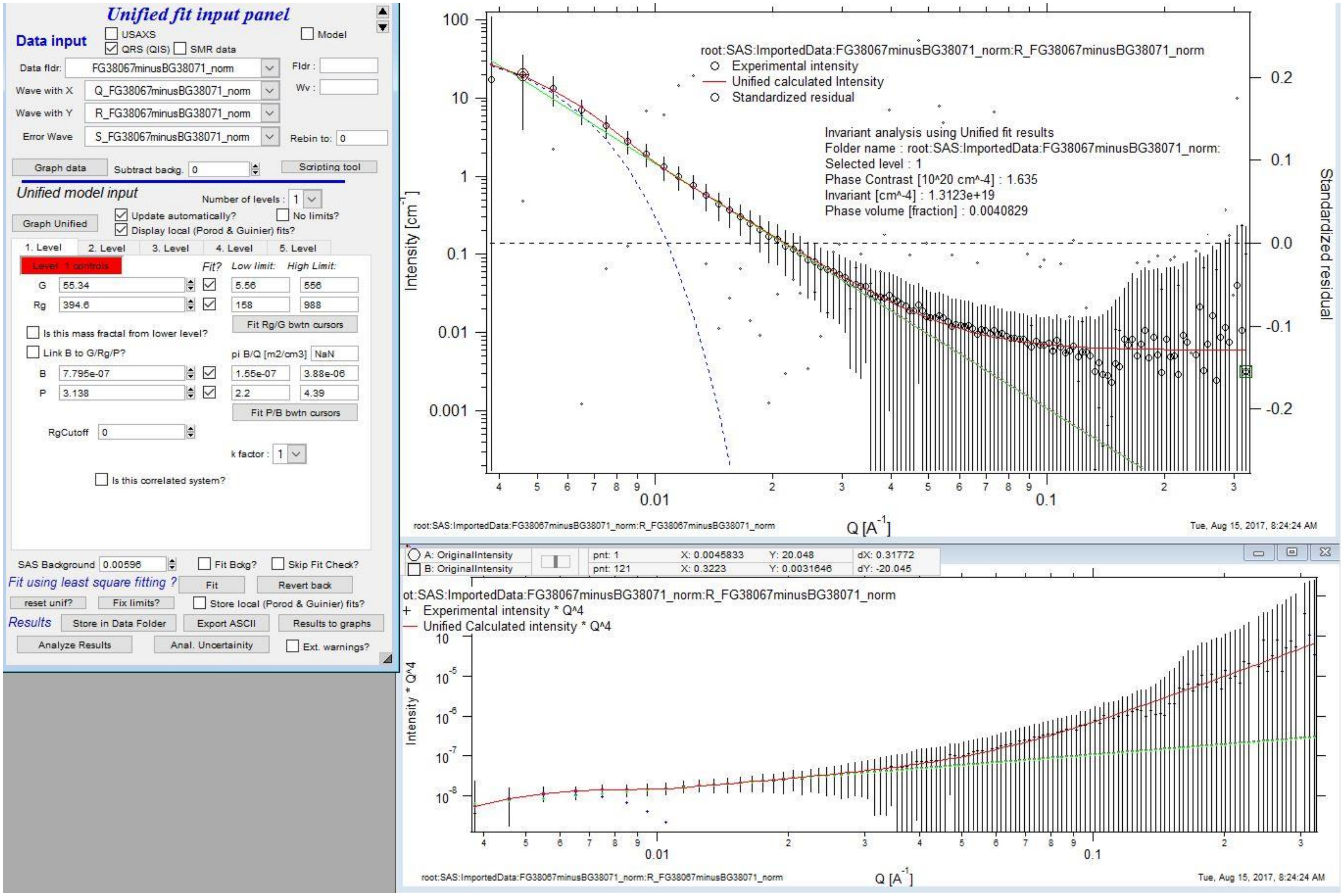


Figure S22. Screenshot of Unified Fit parameters and results for Stage V (sample ID 38067).

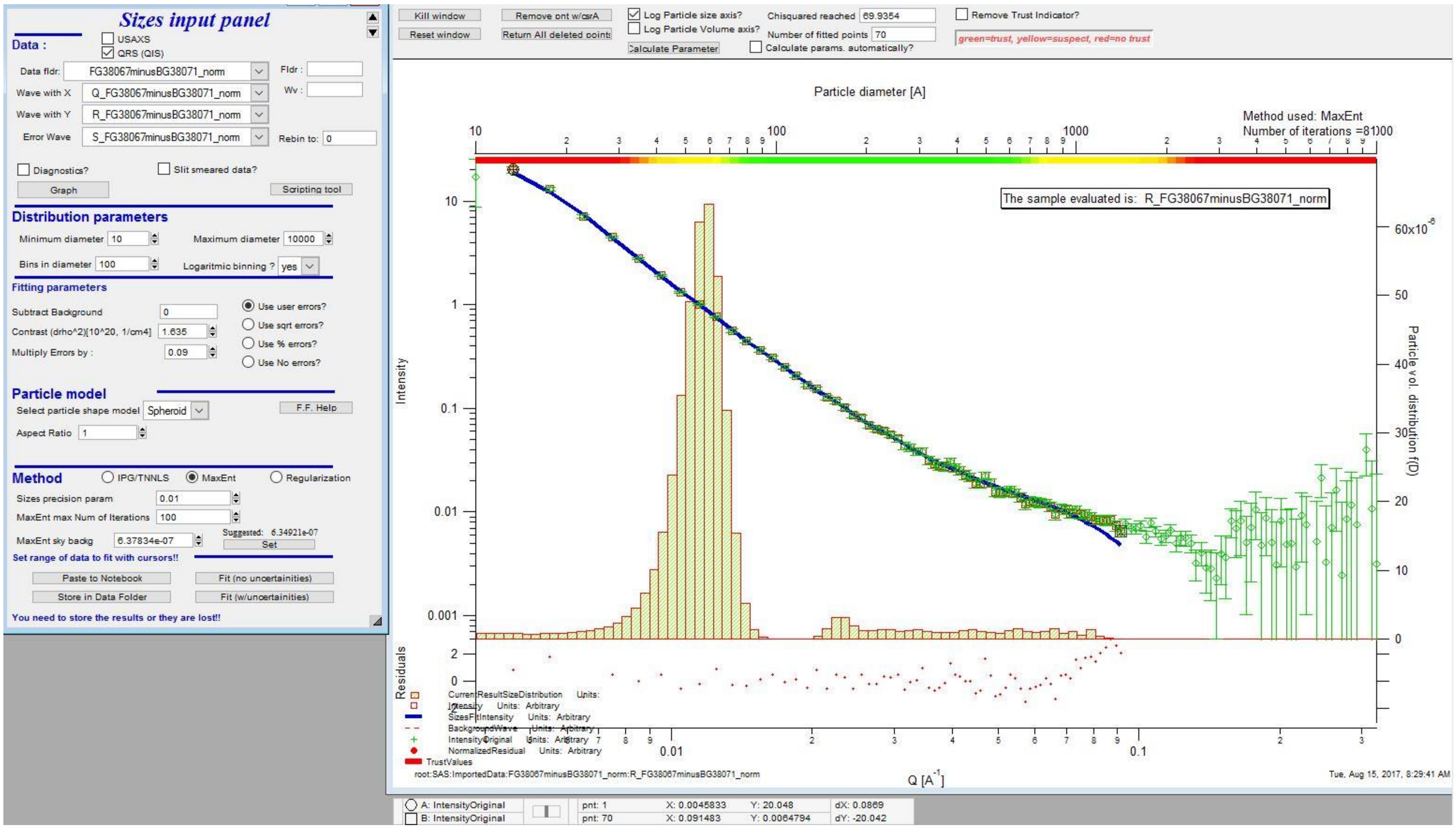


Figure S23. Screenshot of Pore Size Distribution parameters and results for Stage V (sample ID 38067), fit to point 70.

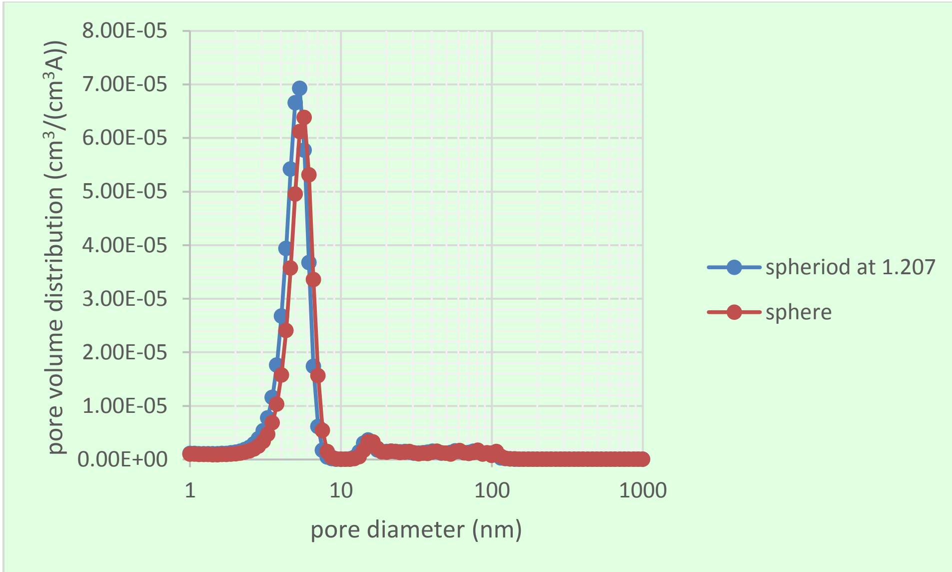


Figure S24. Pore volume distribution for Stage V modeled with spherical pore shapes versus oblate spheroid pore shapes at 1.207 aspect ratio.

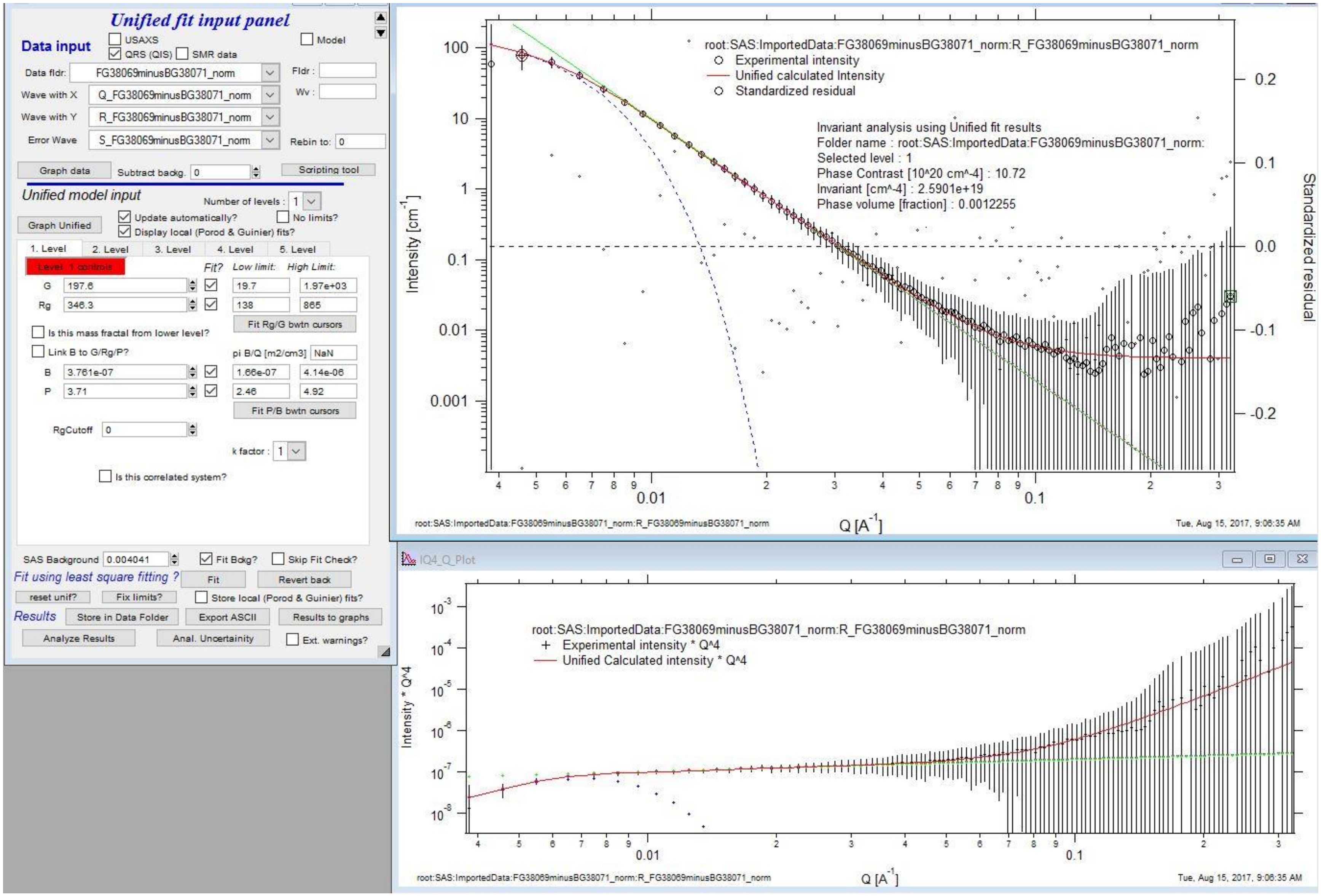


Figure S25. Screenshot of Unified Fit parameters and results for Stage VI (sample ID 38069).

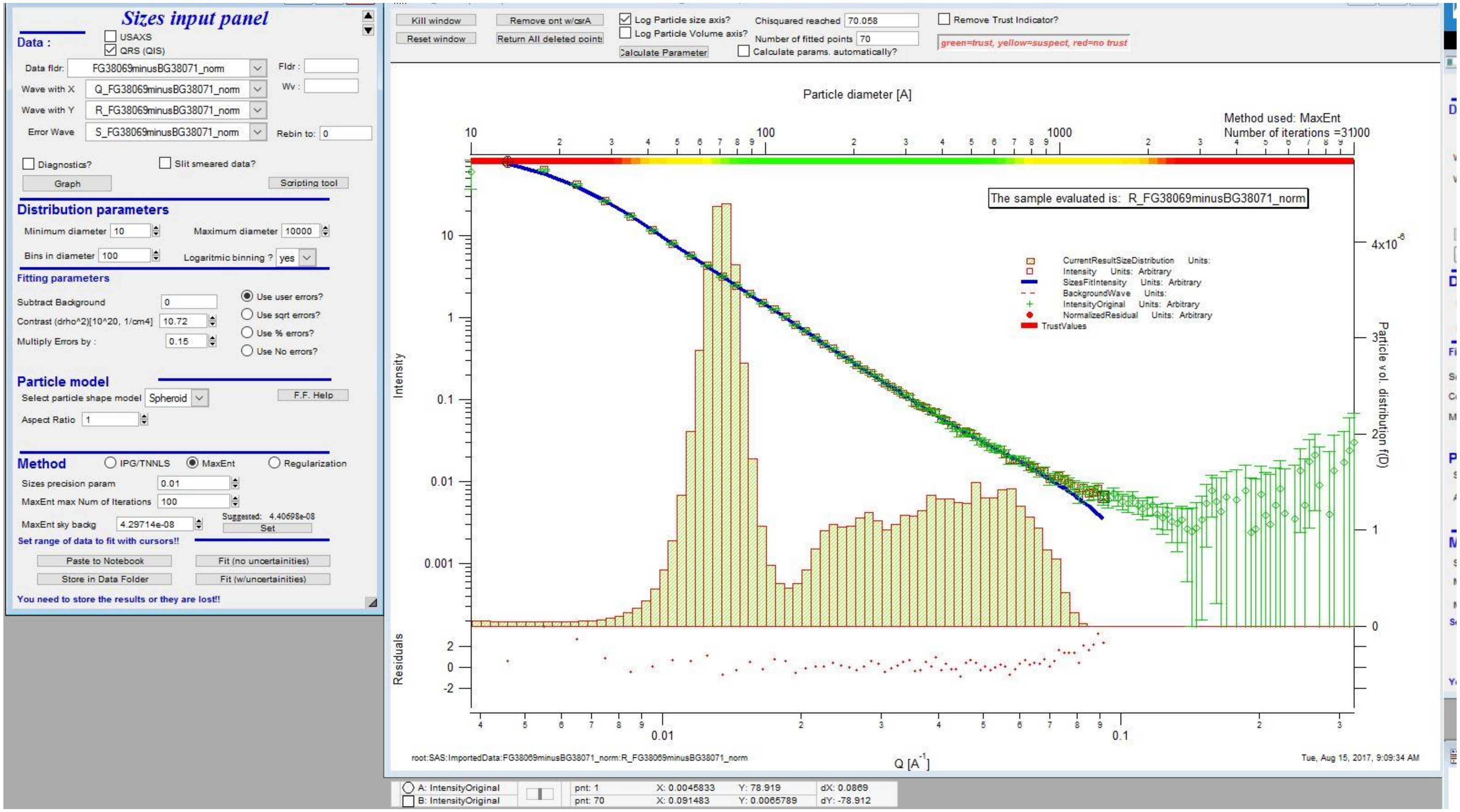


Figure S26. Screenshot of Pore Size Distribution parameters and results for Stage VI (sample ID 38069), fit to point 70.

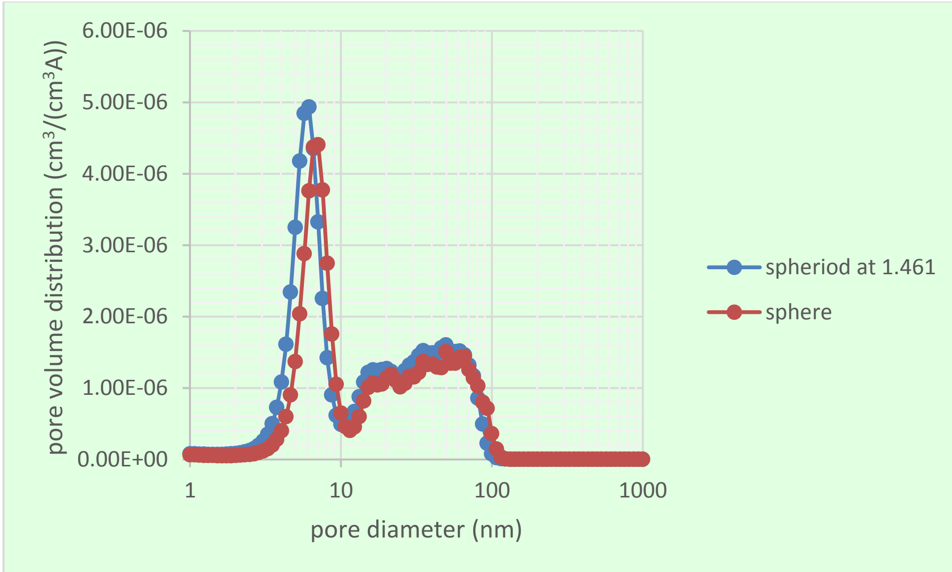


Figure S27. Pore volume distribution for Stage VI modeled with spherical pore shapes versus oblate spheroid pore shapes at 1.461 aspect ratio.

S3.7. Sensitivity of Pore Size Distribution Interpretations to Scattering Contrast.

We assumed in the wet CO_2 stages V and VI that D_2O was dissolved in the CO_2 at saturation. It is possible that the process of flowing wet CO_2 through the sample allowed adsorption or capillary condensation of liquid water in pores. Thus, to assess potential effects of liquid water, we rerun the pore size distributions of Stage V and VI with scattering contrast of 9.582×10^{20} cm^{-4}, which is that of the clay and D_2O at standard atmospheric pressure and temperature (with density of 1.107 g/cm^3). This is a first approximation to see how the pore size distribution would change as interpreted with fully-D_2O saturated pores. Figure S28 (assuming spherical pores) indicates that the height of the peak is greatly increased in the case of liquid D_2O in pores versus D_2O dissolved to saturation in the pores. Figure S29 shows that the liquid D_2O assume for Stage V results in little change in the pore size distribution. The high-pressure CO_2 stages of III and V, for dry and wet CO_2, have similar scattering contrast values of 1.54 and 1.64×10^{20} cm^{-4}, due to the small amount of D_2O that can dissolved in dry and liquid CO_2. Assuming fully saturated pores with D_2O instead of high pressure CO_2 gives much different scattering contrast of 9.582×10^{20} cm^{-4}, which in turn causes a large difference in the pore size distribution (Figure S28). However, for low pressure, the dry and wet CO_2 scattering contrast values are more similar to that of liquid D_2O, with values of ~10.72 versus 9.58×10^{20} cm^{-4}, respectively. Thus, the low pressure dry and wet CO_2 cases do not show a large difference from the case of liquid D_2O in pores (Figure S29).

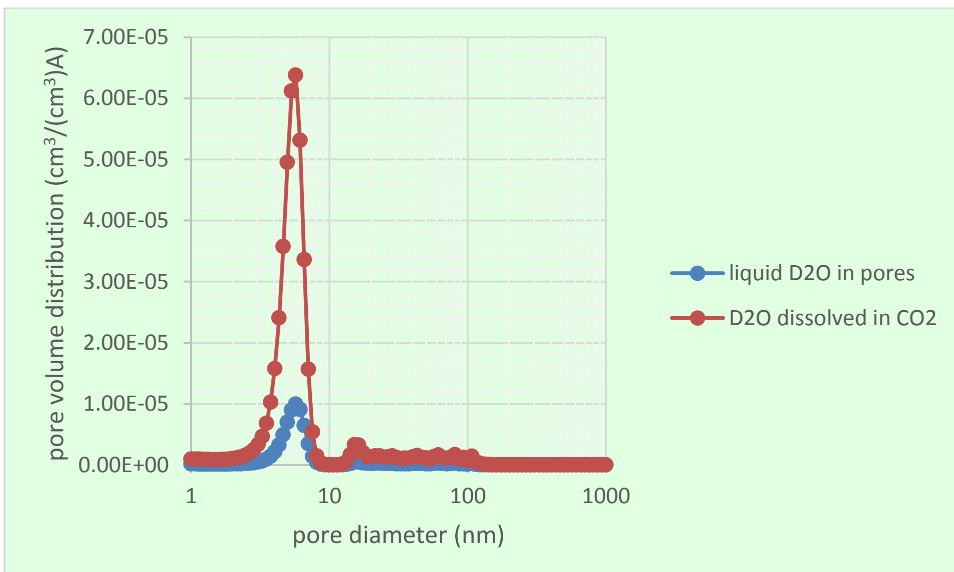


Figure S28. For Stage V, pore size distribution replotted assuming a scattering contrast of liquid D2O and clay versus a scattering contrast of D_2O dissolved in CO_2 at the temperature and pressure of Stage V.

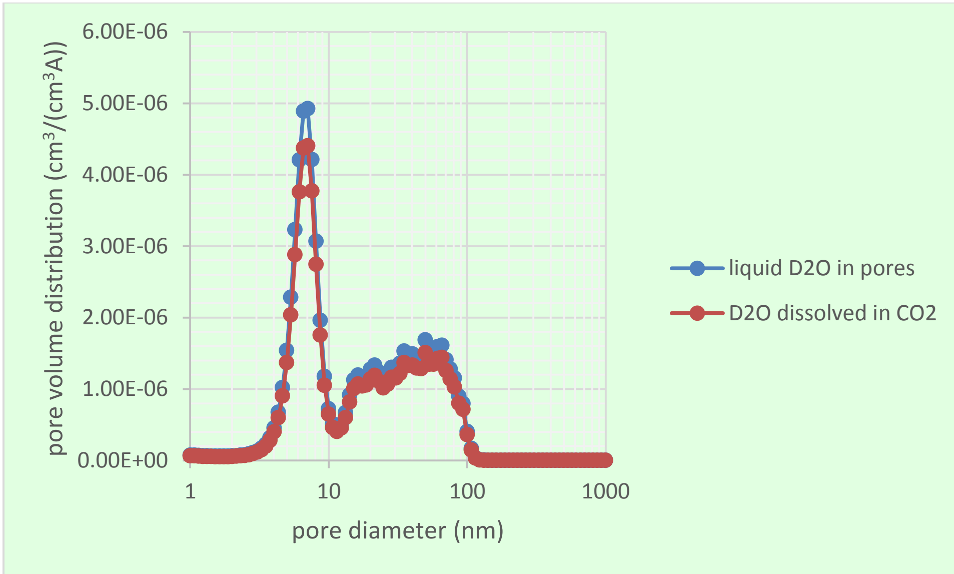


Figure S29. For Stage VI, pore size distribution replotted assuming a scattering contrast of liquid D_2O and clay versus a scattering contrast of D_2O dissolved in CO_2 at the temperature and pressure of Stage V.

S4. TOUGH2 Calculations of Water Saturation and Liquid CO_2 Density, and Calculations of Scattering Contrast

Calculations of scattering contrast require the density of dry and wet CO_2 and the amount of dissolved water in CO_2 at the various pressures and the temperature of 18°C. The density of liquid CO2 at water saturation values at various pressure was obtained using an equation of state for CO_2 as implemented in TOUGH2 (Pruess, 2005). Figure S30 presents the range in TOUGH2-calculated density and saturation of water in CO_2 for the pressure encountered in this study. This can be used to estimate the volume of water available for clay swelling observed in moving from stage IV to stage V in both OSC and TIOC experiments. The mass fraction of water dissolved in liquid CO_2 at the conditions of stage V are seen to be 0.001 $kg_{H2O}/kg_{CO2.}$ (Figure S30). All this water scavenged into smectite interlayer regions would involve a volume of approximately 0.0083 m^3H_2O/m^3CO_2, using interlayer densities of water of 1000 kg/m^3 and liquid CO_2 of 820 kg/m^3. At a void ratio at during stage V observed to be ~0.74 and a total volume of solids of 8.2 cm^3 for TIOC and 0.81 cm^3 for OSC, we calculate a total CO_2 volume of about 6 x 10^{-6} m^3 and 0.60 x 10^{-6} m^3 respectively. The associated volume of water available for swelling would be about 5x10^{-8} m^3 or 5 x 10^{-2} cm^3 for the TIOC test and approximately ten times less for OSC.

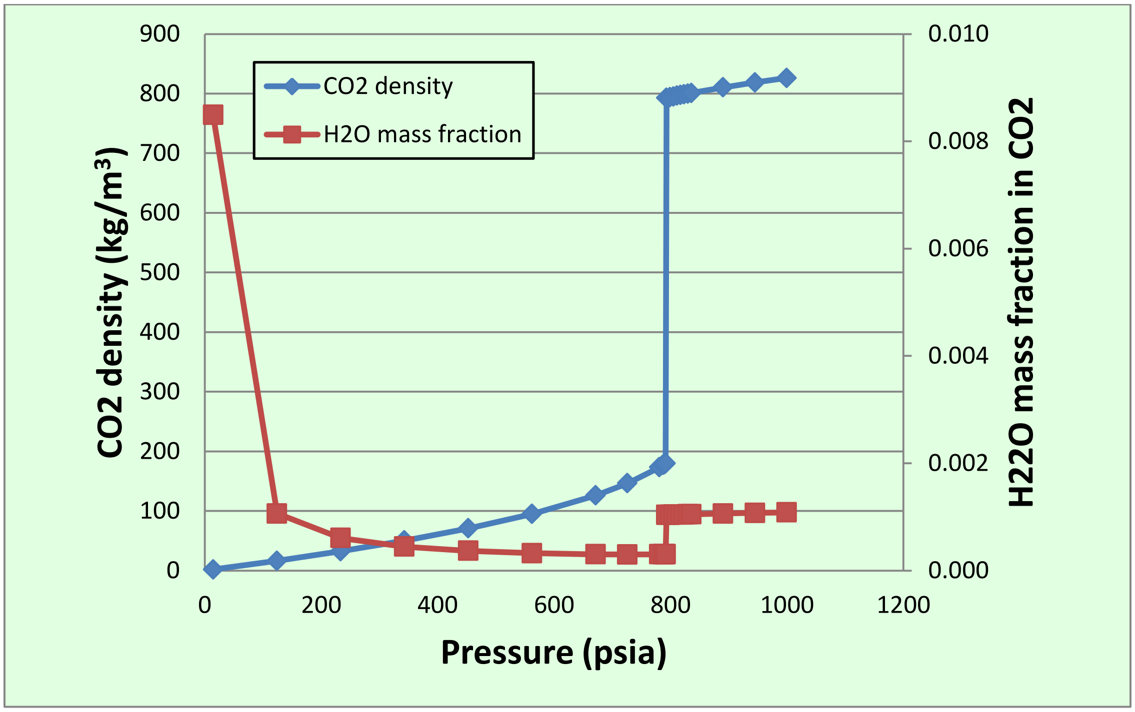


Figure S30. CO_2 density and H_2O mass fraction dissolved in CO_2 as a function of pressure.

The Scattering Contrast Calculator macro of the Irena package was used to calculate neutron scattering length density and scattering contrast for the nitrogen (air), dry and wet CO_2, and SWy-2 environments. Scattering contrast is an input to the Size Distribution macro of Irena that is used to calculate pore size distribution. The main inputs to the scattering contrast calculator are chemical formulas (with integer stoichiometric coefficients) and densities of the substances in questions. For air (nitrogen) and SWy-2, we assume densities of 0.001165 g/cm^3 and 2.3 g/cm^3. For dry and wet CO_2, we obtain densities at the relevant pressures and temperatures, including mass fractions of dissolved water in CO_2, from the TOUGH2-ECO2N code (Pruess, 2005). For the wet CO_2 case, the stoichiometric formula was calculated to reflect the water mass fraction in CO_2. Figures S1-S5 are screenshots of the scattering contrast calculator for the different SANS-oedometer stages that included pairs of SWy-2 with nitrogen and dry or wet CO_2. Specific details for pressure conditions and stochiometric formulas used for wet CO_2 are given in the figure captions.

Table S4. Values of Scattering Length Density and Scattering Contrast

Parameters

	SLD [10^{10} cm^{-2}][a]			
stage	Swy-2	N_2	CO_2	$\Delta\rho^2$[10^{20} cm^{-4}][b]
I	3.279	0.0047	-	10.72
II	3.279	0.0047	-	10.72
III	3.279	-	2.04[c]	1.54
IV	3.279	-	0.0046[c]	10.72
V	3.279	-	2.001[d]	1.635
VI	3.279	-	0.0047[d]	10.72

[a]Neutron scattering length density.

[b]Scattering contrast.

[c]Dry CO_2.

[d]Wet CO_2

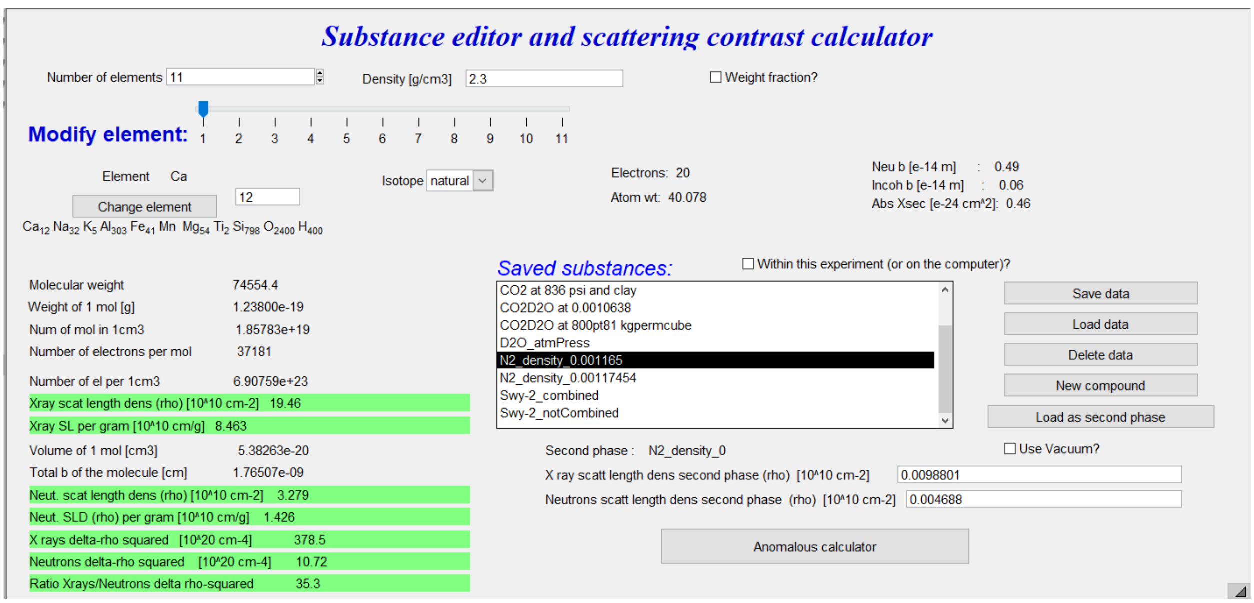


Figure S31. Screen shot of Scattering Contrast Calculator for SWy-2 and N_2, which corresponds with Stages I and II.

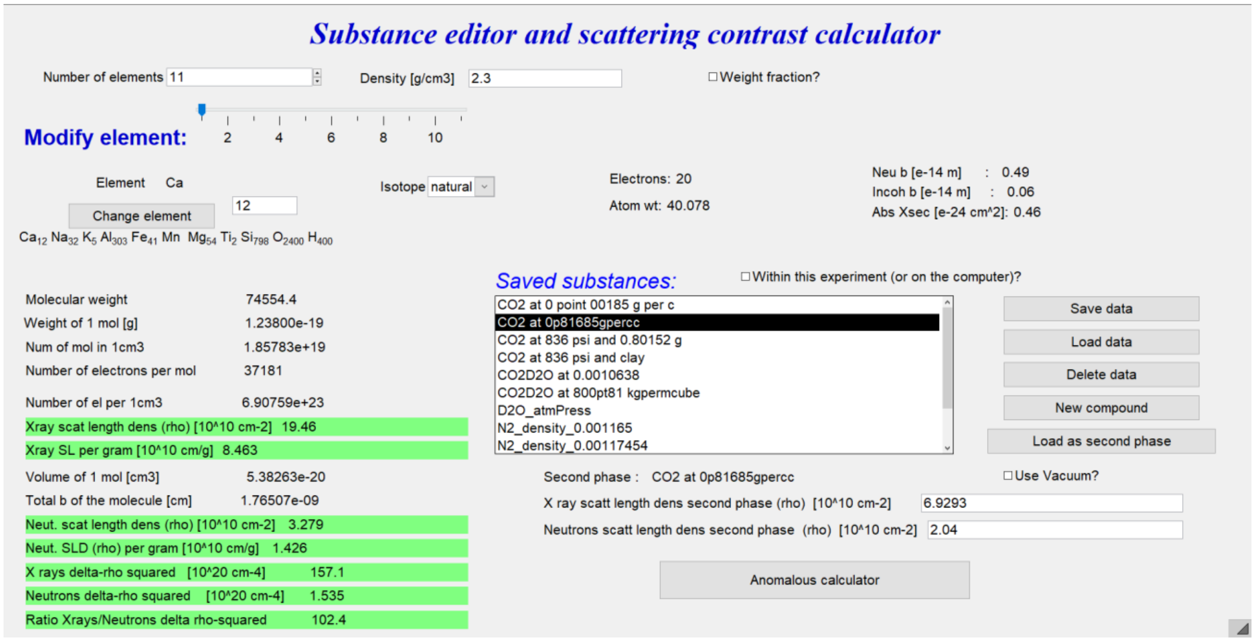


Figure S32. Screen shot of Scattering Contrast Calculator for SWy-2 and pure CO_2 at a density of 0.81685 g/cm^3 (at the pressure of 930 psia), which corresponds with Stage III.

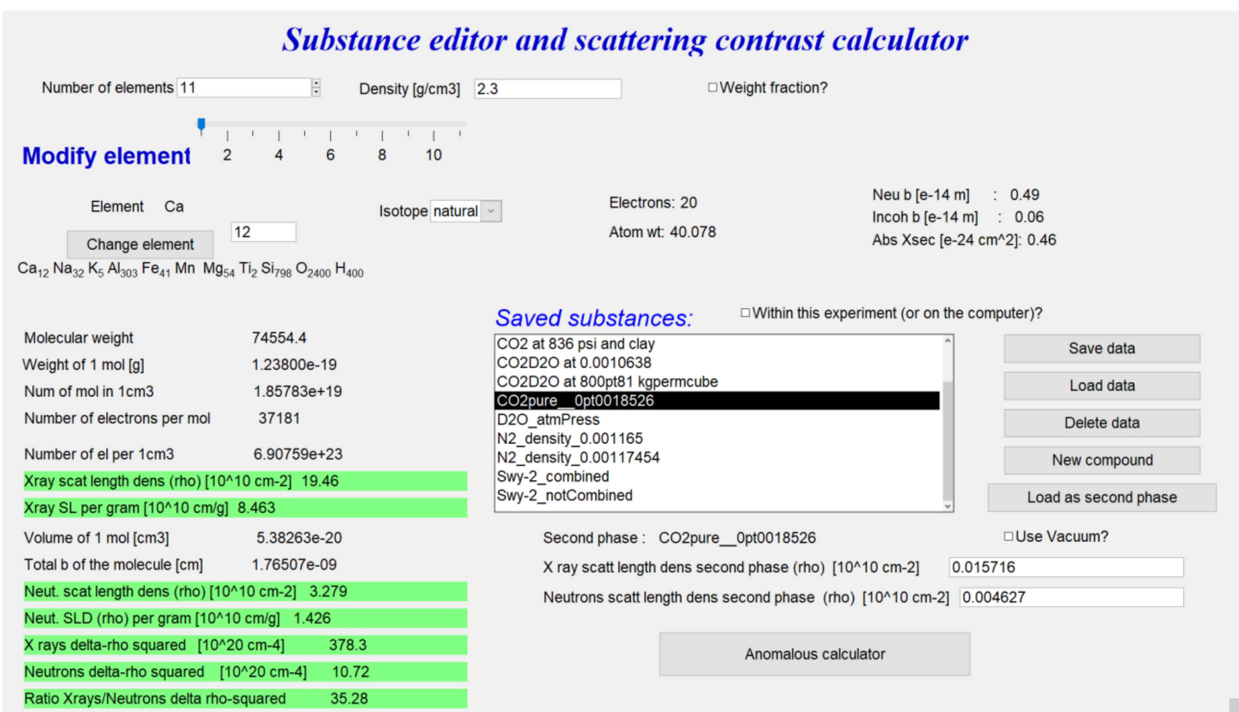


Figure S33. Screen shot of Scattering Contrast Calculator for SWy-2 and pure CO_2 at a density of 0.0018526 g/cm^3 (at the pressure of 14.7 psia), which corresponds with Stage IV.

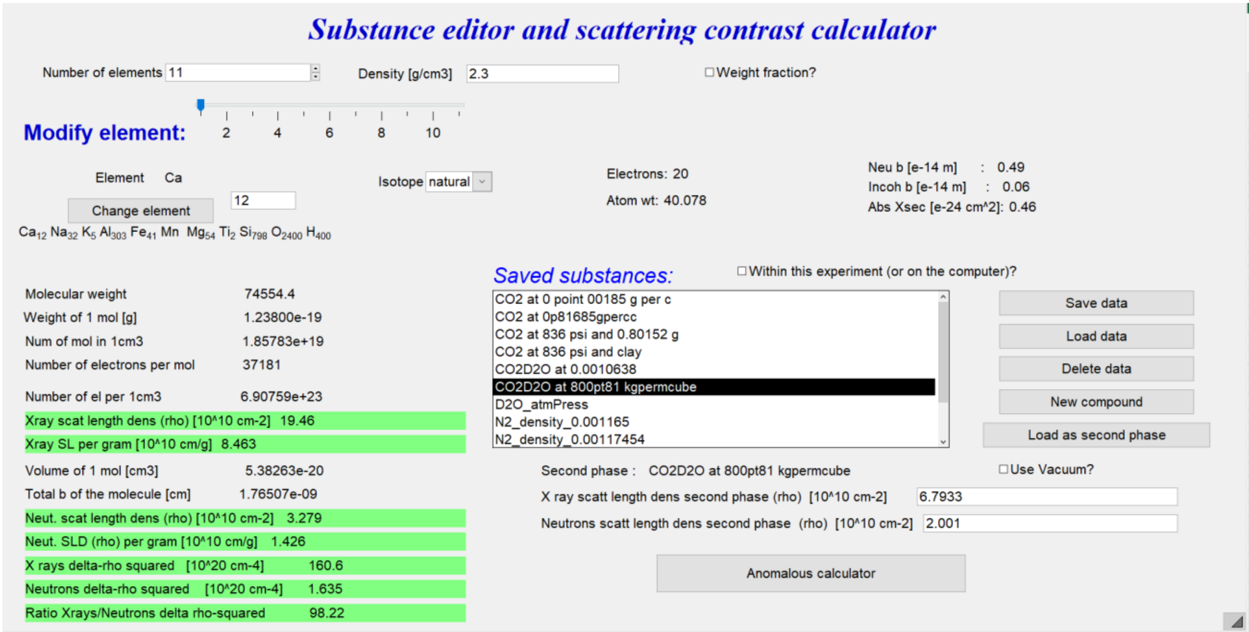


Figure S34. Screen shot of Scattering Contrast Calculator for SWy-2 and wet CO_2 at a density of 0.800810 g/cm^3 (at the pressure of 836 psia) and a mass fraction of dissolved water of 0.0010490, which corresponds with Stage V. The formula for wet CO_2 was determined based on the mass fraction of dissolved water (which needed to be given in integer values), which is C998951O1997902D2098O1049.

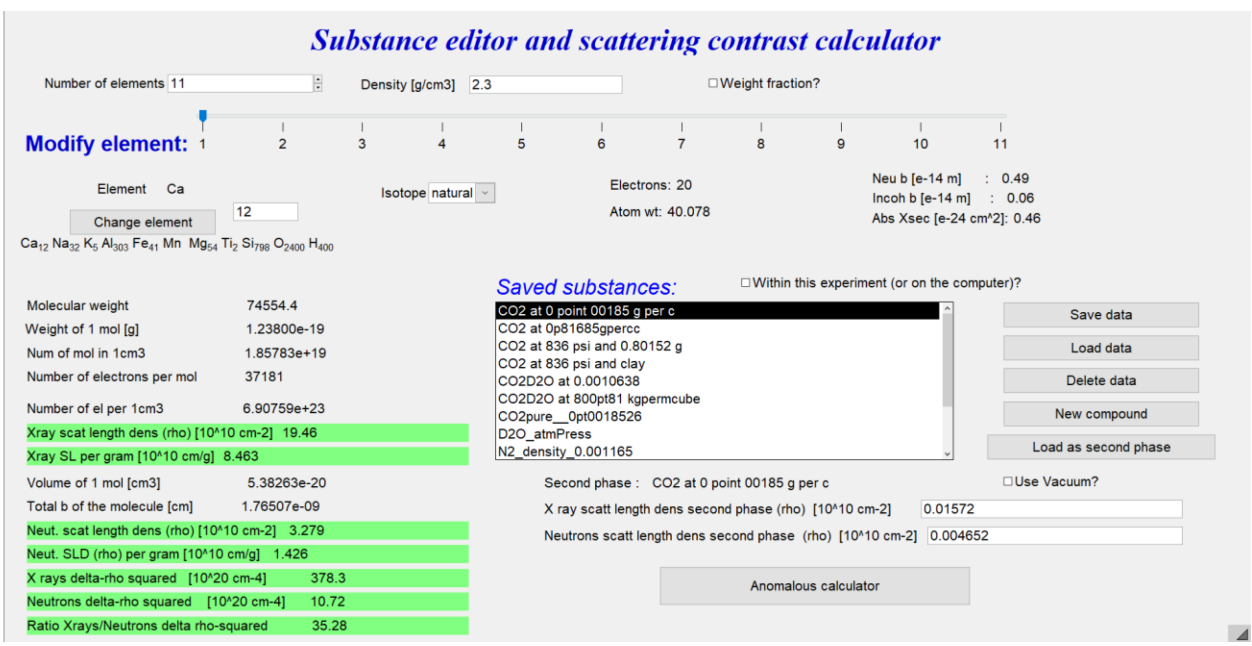


Figure S35. Screen shot of Scattering Contrast Calculator for SWy-2 and wet CO_2 at a density of 0.0018531 g/cm^3 (at the pressure of 14.7 psia) and a mass fraction of dissolved water of 0.00849210, which corresponds with Stage VI. The formula for wet CO_2 was determined based on the mass fraction of dissolved water (which needed to be given in integer values), which is C9915079O19830158D169842O84921.

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Pruess, K. ECO2N: A TOUGH2 fluid property module for mixtures of water, NaCl, and CO2; LBNL-57952; Lawrence Berkeley National Laboratory: Berkeley, CA, 2005; p 66.