

Mineral Resources Program**Energy Resources Program**

Geochemical and Mineralogical Properties of Boquillas Shale Geochemical Reference Material ShBOQ-1

The ShBOQ-1 geochemical reference material is relevant to studies of the organic geochemistry and mineralogy of petroleum source rocks containing high concentrations of carbonate minerals and organic sulfur-rich, oil-prone marine organic matter. ShBOQ-1 is geochemically and mineralogically similar to the lower part of the Upper Cretaceous Eagle Ford Shale.

Introduction

Since 1951, the U.S. Geological Survey (USGS) has developed a number of geochemical reference materials (GRMs) relevant to a wide range of geologic resources. These GRMs provide quality control and experimental materials for USGS researchers as well as for users in industry, academia, and other government agencies. As part of this long tradition of identifying, preparing, and characterizing GRMs, the USGS Mineral Resources Program's Geochemical Reference Materials Project has collaborated with the USGS Energy Resources Program's Petroleum Geochemistry Research Laboratory Project to collect GRMs representative of source rocks from major domestic petroleum systems (Birdwell and others, 2016; Birdwell and Wilson, 2017). These GRMs are meant primarily for use in supporting analytical efforts to characterize the geochemistry and mineralogy of organic-rich mudrocks from petroliferous basins in the United States and around the world.

The GRM data presented here are from the Upper Cretaceous Boquillas Formation (ShBOQ-1) in southwest Texas. The Upper Cretaceous Boquillas Formation (ShBOQ-1) geochemical reference material is relevant to studies of the organic geochemistry and mineralogy of petroleum source rocks containing high concentrations of carbonate minerals and organic sulfur-rich, oil-prone marine organic matter. ShBOQ-1 is geochemically and mineralogically similar to the lower part of the Upper Cretaceous Eagle Ford Shale, which is a major petroleum resource play located in South Texas. The GRM is primarily relevant to marine carbonate source rocks present in a wide range of petroleum systems.

For development of this GRM, a total of approximately 720 kilograms (kg) of carbonate source rock were collected in 2015 at a road cut located approximately 20 miles west of Comstock, Texas, along State Highway 90 (29°42'10.0"N, 101°12'40.1"W); 360 kg of this material was processed for use in the preparation of ShBOQ-1. The ShBOQ-1 GRM has undergone laboratory testing to quantify (1) major and trace element concentrations, (2) total organic carbon (TOC) content, (3) programmed pyrolysis (for example, Rock Eval) parameters, and (4) X-ray diffraction (XRD) mineralogy.



Photograph from a road cut off of US-90 west of Del Rio in Val Verde County, Texas, after collection of ShBOQ-1 material. Photograph by Justin E. Birdwell, U.S. Geological Survey, 2015.

Testing Study Results

A number of commercial, academic, and government laboratories participated in interlaboratory testing studies to generate the averages and standard deviations for a variety of source rock properties presented here. Full datasets are available in an accompanying data release (Birdwell and Wilson, 2021). Major and trace element results from 99 laboratories participating in an international testing study using this GRM conducted by the International Association of Geoanalysts (Webb and others, 2017) demonstrate the homogeneity of the ShBOQ-1 GRM. The results from that study indicate that the reported variability in organic geochemical and mineralogical properties are due primarily to analytical variance and not GRM heterogeneity (Birdwell and Wilson, 2019). Two versions of the material were prepared to accommodate laboratory analysis (<0.074 millimeters [mm]) and well-head studies (<4 mm). The data presented here are applicable to both.

Data from a USGS contract laboratory were used to calculate average values and standard deviations for the elemental concentrations presented here based on replicate analyses using a variety of USGS Minerals Resources Program (MRP) analytical methods (U.S. Geological Survey Mineral Resources Program, 2020). Fourteen replicate analyses were made by each method; these results are summarized in table 1 for major elements and other bulk parameters and in table 2 for selected trace elements. These results are consistent with those reported by Webb and others (2017). The full dataset for the elemental results and other properties summarized in this fact sheet can be found in the accompanying USGS data release (Birdwell and Wilson, 2021).

Table 1. Major element concentrations. Major element concentrations were determined using Mineral Resources Program (MRP) Methods 3, 4, 15, 16, 17, and 18 (U.S. Geological Survey Mineral Resources Program, 2020).

[wt. %, weight percent; LOI, loss on ignition]

Major element oxide and other parameters	Average (wt. %)	Standard deviation	Number of analyses
Silicon dioxide (SiO ₂)	26.21	1.08	42
Aluminum oxide (Al ₂ O ₃)	4.35	0.26	56
Iron (III) oxide, total (Fe ₂ O ₃ T)	1.60	0.05	56
Calcium oxide (CaO)	33.79	0.90	56
Magnesium oxide (MgO)	0.42	0.03	56
Potassium oxide (K ₂ O)	0.42	0.06	56
Sodium oxide (Na ₂ O)	0.04	0.01	42
Phosphorus pentoxide (P ₂ O ₅)	0.10	0.01	56
Titanium dioxide (TiO ₂)	0.18	0.01	56
Total sulfur (S _{tot}) ¹	1.64	0.02	14
Total carbon (C _{tot}) ²	11.26	0.05	14
Inorganic carbon (C _{inorg}) ³	6.65	0.08	14
Organic carbon (C _{org}) ⁴	4.61	0.11	14
LOI ⁵	31.81	0.10	14

¹Total sulfur by MRP Method 3.

²Total carbon by MRP Method 3.

³Inorganic carbon by MRP Method 4.

⁴Organic carbon by difference (C_{tot} - C_{inorg}).

⁵Loss on ignition by MRP Method 15.

Table 2. Selected trace element concentrations. Trace element concentrations were determined using Minerals Resource Program Methods 6, 15, 16, 17, and 18 (U.S. Geological Survey Mineral Resources Program, 2020).

[ppm, parts per million or milligram/kilogram]

Trace element	Average (ppm)	Standard deviation	Number of analyses
Arsenic (As)	14.6	0.4	28
Barium (Ba)	73.0	4.1	42
Beryllium (Be)	0.7	0.1	14
Bismuth (Bi)	0.2	0.03	28
Cadmium (Cd)	2.1	0.1	28
Cerium (Ce)	23.9	0.3	28
Cobalt (Co)	5.9	0.2	28
Chromium (Cr)	30.3	1.9	28
Cesium (Cs)	3.2	0.2	14
Copper (Cu)	37.7	1.1	28
Dysprosium (Dy)	1.6	0.1	14
Erbium (Er)	0.9	0.04	14
Europium (Eu)	0.5	0.02	14
Gallium (Ga)	6.1	0.6	28
Gadolinium (Gd)	2.0	0.04	14
Holmium (Ho)	0.3	0.01	14
Lanthanum (La)	13.0	0.2	28
Lithium (Li)	26.7	2.1	28
Lutetium (Lu)	24.7	0.8	14
Molybdenum (Mo)	50.9	1.4	28
Niobium (Nb)	5.7	0.3	28
Neodymium (Nd)	10.7	0.2	14
Nickel (Ni)	80.6	2.5	28
Lead (Pb)	6.2	0.7	28
Praseodymium (Pr)	3.0	0.04	14
Rubidium (Rb)	16.7	0.8	28
Antimony (Sb)	3.3	0.1	28
Scandium (Sc)	3.3	0.2	14
Samarium (Sm)	2.1	0.1	14
Tin (Sn)	2.4	1.5	28
Strontium (Sr)	1,049.1	51.2	42
Terbium (Tb)	0.3	0.01	14
Thorium (Th)	2.8	0.1	28
Thallium (Tl)	2.9	0.2	28
Thulium (Tm)	0.2	0.01	14
Uranium (U)	9.1	0.4	28
Vanadium (V)	376.4	37.3	28
Yttrium (Y)	9.3	0.5	28
Ytterbium (Yb)	0.9	0.04	14
Zinc (Zn)	105.2	4.2	28
Zirconium (Zr)	52.5	1.7	28

An interlaboratory testing study was conducted to obtain measurements of TOC content by combustion and infrared analysis and to obtain results from a variety of programmed pyrolysis instruments (Rock Eval 2, Rock Eval 6, Source Rock Analyzer, Hydrocarbon Analyzer with Kinetics) using the same standardized temperature program (Espitalie and others, 1977). Programmed pyrolysis also generates measured values that are used to calculate indices relevant to hydrocarbon-generating potential, thermal maturity, and organic matter type (Peters, 1986). The results of these tests (table 3) present averages and standard deviations that were determined after removing outlier datapoints. Outliers were

identified for each measured parameter by calculating upper and lower limits using the interquartile range (IQR; acceptance range = average \pm 1.5 \times IQR). After removing outliers, the calculations and outlier-removal steps were repeated until all remaining values fell within the acceptance range. This analysis was also performed on the other datasets presented here, but no outliers were identified.

To optimize drilling and hydraulic fracturing operations, in addition to understanding organic properties, it is important to understand mineralogy in unconventional oil and gas plays. Table 4 presents results from interlaboratory tests to determine XRD mineralogy.

Table 3. Organic geochemical measurements and calculated properties from interlaboratory testing study. Extractable organic matter was obtained by extraction with chloroform using a U.S. Geological Survey standard operating procedure.

[wt. %, weight percent; S, sommet (peak in French); mg, milligram; g, gram; Tmax, maximum temperature; °C, degrees Celsius; TOC, total organic carbon; NA, not applicable]

Parameter	Average	Standard deviation	Total number of analyses	Total after outlier removal
Measured values				
Total organic carbon, wt. %	5.09	0.18	156	152
Extractable organic matter, wt. %	0.89	0.03	14	NA
S1, mg-hydrocarbon/g-rock ¹	1.27	0.11	114	112
S2, mg-hydrocarbon/g-rock ¹	31.59	2.57	114	108
S3, mg-carbon dioxide/g-rock ¹	0.70	0.08	114	90
Tmax, °C ¹	424	1.1	114	92
Calculated parameters ¹				
Hydrogen index, S2/TOC \times 100	594	21	NA	NA
Oxygen index, S3/TOC \times 100	14	2	NA	NA
Oil saturation index, S1/TOC \times 100	25	2	NA	NA

¹For details on programmed pyrolysis measured and calculated parameters, see Peters (1986).



Photograph of preliminary materials (“ShBOQ-proto”) used for initial analyses to confirm Boquillas Shale compositional characteristics prior to interlaboratory testing. From left to right: rock powder, pressed pellets (not available), cutting-size chips, and slab piece. Photograph by Stephen A. Wilson, U.S. Geologic Survey, 2016.

Table 4. Mineralogy results from interlaboratory testing study. All values are reported on an organic-free basis and do not account for noncrystalline phases.

[wt. %, weight percent]

Mineral	Average (wt. %)	Standard deviation	Total number of detections ¹
Calcite	64.4	2.9	29
Dolomite	1.1	0.8	29
Quartz	22.8	2.1	29
Kaolinite	6.9	1.9	23
Illite/mica	1.8	0.6	18
Gypsum	2.4	1.0	23
Pyrite	1.4	1.1	29

¹Total number of analyses in which the particular mineral was detected.

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