

Sulfur differentiation in siliceous shales by means of advanced open-system programmed pyrolysis methods: new insights into the hydrocarbon potential and sulfur risk assessment of the Onnagawa Formation from Akita Prefecture, Japan

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Siliceous shales are important source rocks for oil and gas in the North Pacific Sea region. These source rocks can include kerogen enriched in organic sulfur (type IIS kerogen with atomic $S_{org}/C > 0.04$). Due to the different petroleum generation kinetics of type IIS and Type IS kerogens, these source rocks can generate oil at lower thermal maturities than sulfur-lean Type I and Type II.

Twenty samples from the Onnagawa Formation's siliceous shales, Akita Prefecture, were collected from a 42 m-long core and analyzed with the new Rock-Eval 7S analyzer. The Rock-Eval 7S provides estimate of sulfur species (i.e., organic vs. inorganic), hydrocarbon potential, and kerogen type [1]. A new screening parameter, named Sulfur Index (SI= pyrolysis $S_{org}/TOC \times 1000$), is used in tandem with the Hydrogen Index (HI) to differentiate sulfur-rich kerogens (Type IIS, Type IS) from their sulfur-lean counterparts.

Based on Table 1 results, the Onnagawa Formation contains moderate amounts of total organic and pyritic sulfur, and low amounts of sulfate sulfur. The majority of S_{org} is associated with the reactive and thermally labile portion of the TOC (S2-Sulfur or S2-S). TOC, S2, and HI ranges suggest a fair to very good potential for the generation of hydrocarbons and the prevalence of kerogen type IIS, Type II, and mixed II/III. SI values greater than 100 mg/g TOC (equivalent to $S_{org}/C > 0.04$) indicate that most of the analyzed samples are enriched in reactive organic

sulfur (Type IIS and Type IS). Although T_{max} values indicate immaturity for hydrocarbons generation, the sulfur enrichment in the kerogen suggests that the Onnagawa Formation has the potential to generate oil at relatively low thermal maturity. The high SI values in 14 samples analyzed indicate that there is sufficient S_{org} present to potentially produce H_2S from the decomposition of the Type IIS kerogen in the Onnagawa under the right conditions.

References

[1] Carvajal-Ortiz, H., Gentzis, T., Ostadhassan, M., 2021. Sulfur Differentiation in Organic-Rich Shales and Carbonates via Open-System Programmed Pyrolysis and Oxidation: Insight Into Fluid Sourcing and H_2S Production in the Bakken Shale, United States. *Energy & Fuels*, 35, 12030–12044.

Table 1: Rock-Eval 7S data of the Onnagawa Formation discussed in the abstract.

Sample ID	TOC wt. %	TOS wt. %	Fe-S wt. %	Sulfate-S wt. %	S2-S wt. %	S2 mg HC/g	T_{max} °C	SI $PyS_{org} \times 1000/TOC$	HI $S2 \times 100/TOC$
OG1	3.26	0.58	1.17	0.14	0.50	14.90	398	144	457
OG2	1.53	0.64	0.59	0.13	0.41	4.44	402	333	290
OG3	1.88	0.36	0.84	0.13	0.28	5.93	405	154	315
OG4	1.41	0.48	0.43	0.23	0.31	4.04	400	277	287
OG5	2.73	1.15	0.83	0.53	0.46	9.41	406	337	345
OG6	2.11	0.36	0.80	0.13	0.34	9.98	383	137	473
OG7	1.90	0.19	0.60	0.09	0.17	9.40	405	79	495
OG8	2.82	0.34	1.17	0.22	0.29	14.02	397	96	497
OG9	2.90	0.29	0.76	0.18	0.30	16.30	401	79	562
OG10	1.30	0.13	0.40	0.11	0.16	6.15	400	77	473
OG11	3.58	0.58	1.00	0.16	0.53	18.21	399	131	509
OG12	2.32	0.29	0.88	0.16	0.32	10.79	397	99	465
OG13	1.99	0.29	0.39	0.10	0.29	10.39	399	116	522
OG14	1.21	0.11	0.20	0.10	0.12	7.58	400	66	626
OG15	2.17	0.50	2.09	0.19	0.41	7.64	399	184	352
OG16	1.71	0.43	0.67	0.12	0.40	5.84	400	199	342
OG17	1.92	0.72	0.61	0.21	0.44	4.43	405	219	231
OG18	1.58	0.49	0.38	0.10	0.48	6.19	403	247	392
OG19	1.37	0.32	0.62	0.10	0.31	4.64	405	182	339
OG20	1.46	0.42	0.44	0.14	0.32	3.92	405	226	268