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Updated Geochemical Characterization of Hydrocarbon Potential of Surface Sample in Lariang-Karama Sub-Basin, West Sulawesi, Indonesia

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ABSTRACT - The lariang-karama sub-basin is situated within the Makassar basin, located in the West Sulawesi region. It has source of rocks which has the potential to produce hydrocarbons and to become a target for new field discoveries in hydrocarbon exploration activities. It is on this basis that the authors are interested in conducting research in the Makassar basin area and its surroundings, which has been carried out since 2017. This is a comprehensive literature review study from 2017 to 2022, focusing on the origin and composition of biomarkers, paleogeography of facies sources from oil seeps (2017-2018), paleofacies and biomarker characteristics of Paleogene to Neogene rocks (2019), contribution of terrestrial materials based on geochemical and biostratigraphic analysis (2020), tectonic processes occurring in the basin, and geochemical characterization of source rocks in the research area (2022). The FS-12 surface sample in shale may belong to the Kalumpang Formation, located in West Sulawesi. The results of TOC analysis were 0.62%, indicating sufficient quantity. Based on the results of the cross plot between HI values of < 50 and Tmax of 499 °C, the category was found to be overmature and could not produce hydrocarbons. The results of this research, along with those of previous research and the latest geochemical study, were obtained in the West Sulawesi region and the eastern Makassar Strait. These findings consisted of marine shale source rocks in West Sulawesi and lacustrine shale source rocks in the eastern Makassar Strait.

Keywords: source rock, West Sulawesi, total organic carbon (TOC).

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INTRODUCTION

Hydrocarbons play a very important role as an energy resource to support the Indonesian economy (Praptisih 2022). Exploration of hydrocarbons is a crucial activity in the oil and gas sector that involves searching for new reserves to meet production needs and developing existing oil fields. An essential component of exploration is geochemical analysis, which can be carried out on surface samples and hydrocarbon seeps. Various geochemical analyses have been conducted on surface samples and seeps in WestSulawesi. In research by (Sutadiwiria et al. 2017 ,2018) on oil seeps in the Lariang and Karama areas of West Sulawesi, the oleanane saturation found in these seeps indicates that the source rocks in the West Sulawesi area were formed in delta and near-coastal environments. This oil seep is known to originate from Eocene coal and Toraja shale coal from the Kalumpang formation. The results of biomarker analysis on GC-MS show that the source of oil seep in Lariang can be traced back to terrestrial organic material, with the additional presence of organic materials from algae and herbs (Sutadiwiria 2019).

The Lariang-Karama sub-basin in the Makassar basin has the potential to produce hydrocarbons. This study aims to refine the predictions regarding the capacity of the area's source rock to produce hydrocarbons by using geochemical analyses of hydrocarbons. These analyses determine the quality of organic materials from rock-eval pyrolysis (REP), the quantity of organic materials from total organic carbon (TOC), the degree of maturity of the hydrocarbon from cross-plot Tmax vs HI, gas chromatography (GC), and gas chromatography/ massspectrometry (GC/MS).

Regional Geology

Makassar basin is located in Indonesia and is bounded by different geographical features. To the north lies the Mangkalihat High, while the Java Sea is situated in the south. In the west, it is bordered by the East Kalimantan mainland, which includes the Mahakam Delta and the SSW-NNE fold structure. On the east, it is bounded by the mainland of West Sulawesi, which has a thrust fold in the SSW-NNE direction. The Makassar basin was formed during the pre-Tertiary to late tertiary extensional stages, which occurred no earlier than the early paleocene (Sutadiwiria et al. 2022). Calvert & Hall (2003) have reported that the research area is located in the eastern part of the Makassar Basin. The basin was formed during the early tertiary, paleocene, and middle Eocene-Late Eocene. This formation was due to its expansion. The rifting led to the formation of graben and half-graben, and the subsidence formation took place during the early period of the rifting. This process caused the island of Sulawesi to move from east to southeast and separate from the mainland of Sunda/Kalimantan. The area is subjected to extensional compressional forces, which have led to the upliftment, folding, and shearing of the pre-tertiary basement, resulting in the formation of rock depressions and elevations (Figure 1).

Regional Tectonic

The Makassar basin, where the Lariang-Karama Sub-Basin is formed, has three main fault patterns: northeast-southwest, northwest-southeast, and north-south. According to (Fraser 2003, Calvertand Hall 2007, and Raharjo et al. 2012), the formation of Makassar basin can be divided into six tectonic stages (Figure 2). These stages are the Pre-rift stage (pre- Tertiary), Syn-rift package stage (Middle-Late Eocene), Post-rift package stage (Oligocene), Post-rift package stage (Early-Middle Miocene), Post-rift package stage (Late Miocene) and Foreland basin package stage (Early-recent Pliocene).

Regional Stratigraphy

The study area is marked on a stratigraphic column (Calvert & Hall 2003; Raharjo et al. 2012) (Figure 2). The area is part of the Lariang-Karama Sub-Basin, which is situated in the eastern region of Makassar Basin. The geological formations in the area are arranged in the following order from the oldest to the youngest. Basement (Mesozoic) is composed of metamorphic rocks, black shale, and volcanic rocks. Kalumpang Formation (Middle Eocene-Late Eocene) consists of claystone, carbonate shale, coal seams, siltstone, and quartz sandstone. Budung-budung formation (Middle Eocene-Early Miocene) consists of shale, shaly mudstone, coal, siltstone, clastic limestone, and conglomerate. The lisu formation consists of early-late miocene mudstone, sandstone, and layers of volcanic product debris and tuff. The Pasang kayu formation (early pliocene pleistocene) consists mainly of conglomerate and layers of sandstone and mudstone. Based on regional geology, (Calvert & Hall 2007 and Raharjo et al. 2012) identified the source rocks in West Sulawesi into two potential formations: the eocene Kalumpang formation and the miocene Budung-Budung formation. According

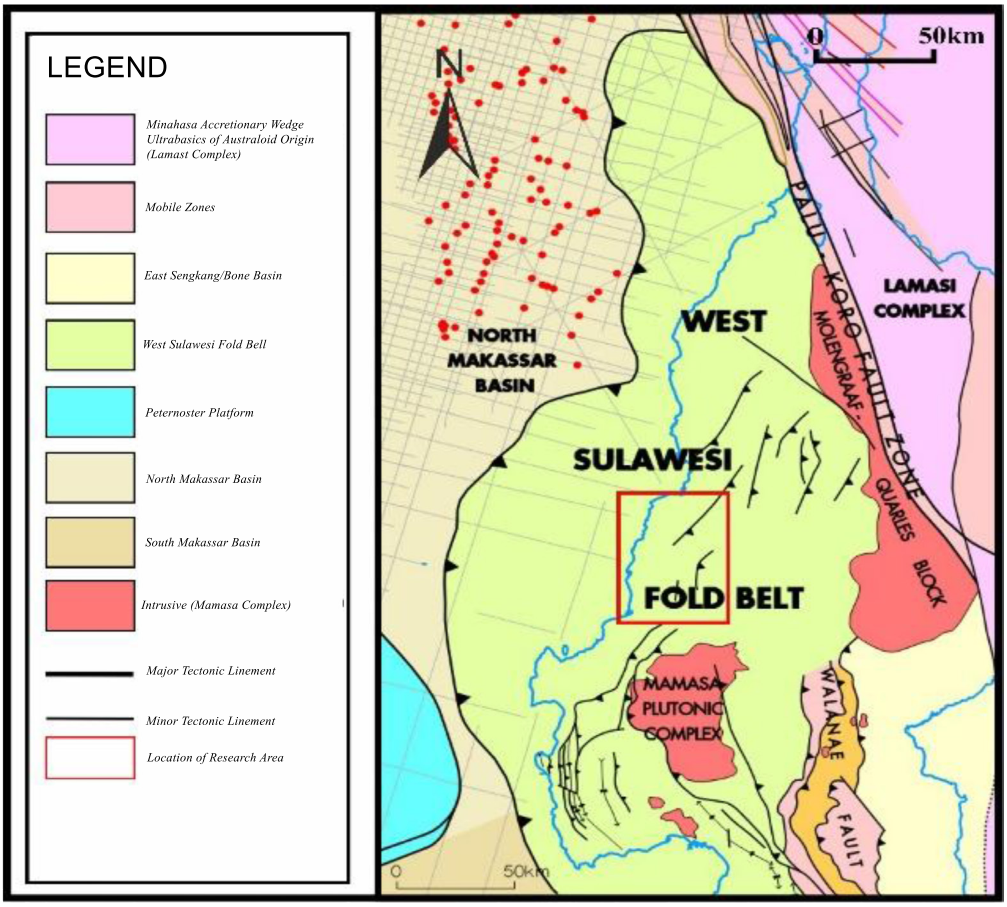

Figure 1
The tectonic setting that influences the Makassar Basin (Fraser 2003)

to (Waples 1985), source rocks can be classified into three groups: effective source rock, possibles ource rock, and potential source rock. Effective source rock is formed by organic materials which can accumulate and generate hydrocarbons. Possible source rock has the potential to store and produce hydrocarbons, but it has not been evaluated. On the other hand, potential source rock is immature but can store and produce hydrocarbons as it matures.

METHODOLOGY

This research involved the use of geochemical analysis, including total organic carbon (TOC) measurement, rock-eval pyrolysis analysis, cross-plotting Tmax vs HI and HI vs OI for hydrocarbon maturity assessment, gas chromatography (GC), and gas chromatography/mass spectrometry (GC/MS). Additionally, Microsoft Excel software was used to generate graphs. The geochemical analysis was carried out in the geochemical laboratory of PT. Geoservices, and the standard laboratory methods have been internationally recognized according to ISO 900:2015. The results of this study were combined with the findings of previous studies to provide an updated and comprehensive geochemical analysis for the West Sulawesi region.

Total Organic Carbon (TOC)

TOC is the quantity of organic carbon deposited in the rock which is expressed as a percentage of the weight of the dry rock. Organic carbon is carbon that comes from organic substances and does not come from carbonates, for example limestone. The total organic carbon (TOC) value is determined by analyzing the sample data and obtaining numerical results. Sedimentary rocks that contain a TOC value of 0.5% or lower are considered to have a very low potential to produce hydrocarbons. On the other hand, rocks that have the potential to be a source rock contain a TOC of >0.5% as per (Peters 1994) Table 1.

Table 1
Source rock quality parameters based on TOC (Peters 1994)

Quality	TOC (w.t%)
Bad	< 0.5
Fair	0.5 – 1
Good	1 – 2
Very Good	2 – 4
Excellent	> 4

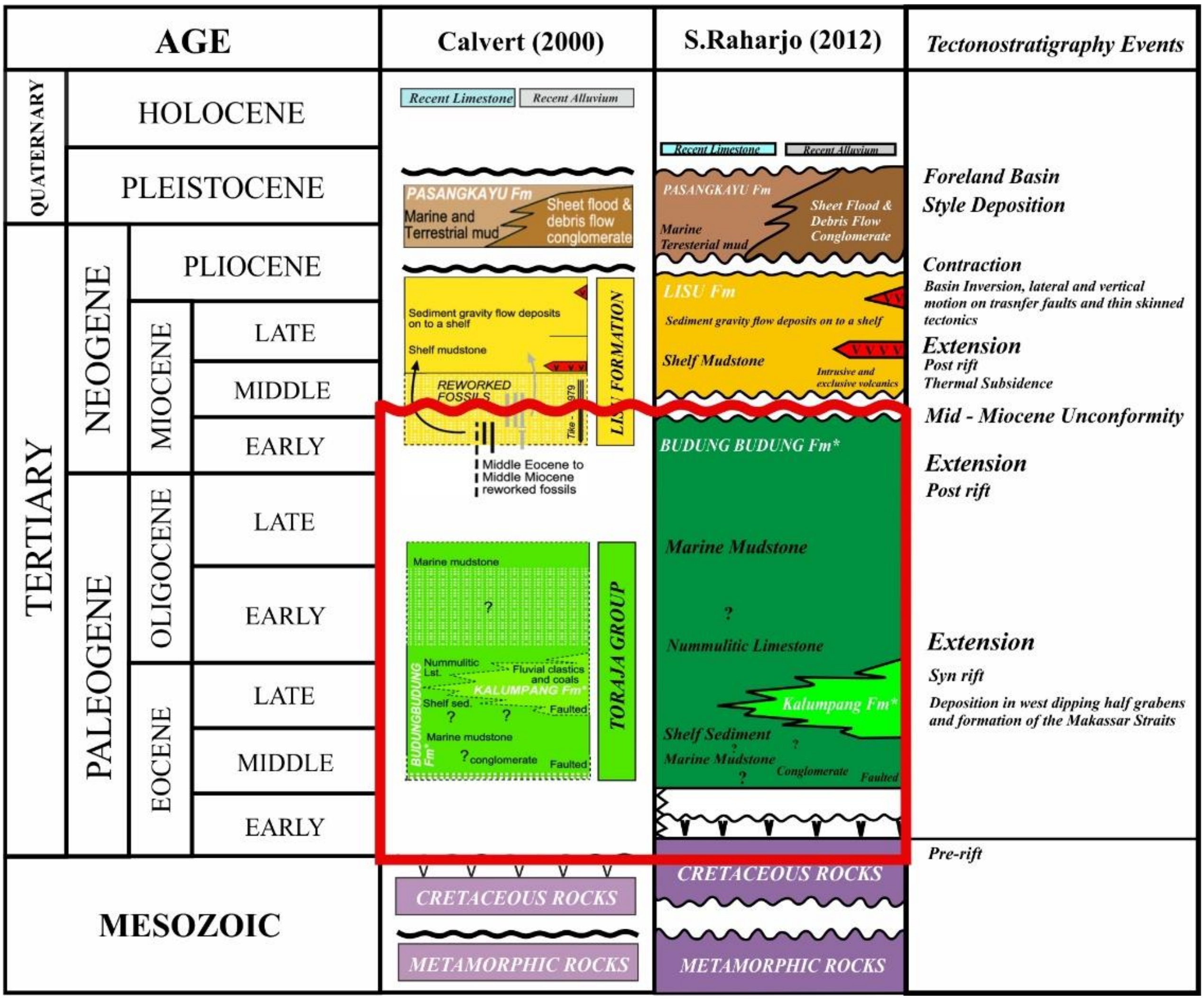

Figure 2
Modified Mamuju Regional Stratigraphic Column, West Sulawesi (Calvert & Hall 2003 and Raharjo et al. 2012)

Kerogen Type

Kerogen is the organic material present in source rocks that produce oil and gas. It plays a significant role in determining which hydrocarbons will beformed. Kerogens can be classified into different types based on the combination of chemical elements that it contains, such as carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S). The methodused to classify kerogen types is the use of the Van Krevelen diagram (Peters & Moldowan 1993), which involves plotting the hydrogen index (HI) against the oxygen index (OI)atoms. Additionally,a comparisonis made between HI and Tmax values.

Rock–Eval Pyrolysis (REP)

The parameters used to determine the type of kerogen, oil, and gas products are formed at peak maturity (Peters & Cassa 1994). The pyrolysis parameters used to determine the type of hydrogen are the hydrogen index (HI) and the relationship between the ratio of S2 (a hydrocarbon formed from kerogen in rock-eval pyrolysis due to the decomposition of kerogen) and S3. Figure 3 illustrates an analysis of rock-eval pyrolysis in the study area based on (Soppanata 1996).

According to (Hunt 1996), Rock-Eval pyrolysis analysis is based on several parameters. S1 (free hydrocarbons) indicates the number of free hydrocarbons that can be vaporized with out kerogen degradation. It is formed at 300 °C, resulting from kerogen during deposition. S2 (pyrolisable hydrocarbon) indicates the number of hydrocarbons produced through the cracking process. It is formed at a temperature of 350–550°C. S3 shows the amount of CO_2 contentin the rock. It is formed at 300–390 °C. Tmax shows the maximum temperature at the time of the formation of hydrocarbon cracking (S2). It is formed at 435–470 °C.

Maturityof Organic Material

The maturity of organic materials was assessed using two parameters: Tmax and Vitrinite Reflectance(Ro). The tmax value indicates the temperature at which hydrocarbons are formed through cracking (S2) and reach their maximum intensity. Generally, this occurs at 435-470 °C, known as the oil window. On the otherhand, Ro is a parameter that indicates the increase in temperature and its effect on the reflectance of vitrinite. As the temperature rises, the reflectance gloss of vitrinite maceral willalsoincrease. Table 2 provides more information on Ro and its relationship with temperatures.

Gas chromatography (GC) and/or gas chromatography mass spectrometry (GC-MS) analyses were also used in this study. Saturate samples were subjected to gas chromatography (GC) to determine the distribution of isoprenoids and n-alkanes. In the meantime, compounds with low concentrations that could not be separated by gas chromatography (GC) were separated using gas chromatography mass spectrometry (GC-MS) (Waples & Curiale 1999).

The study utilized new data obtained from a surface sample called FS-12, which was taken from the Mamuju area in the Lariang-Karama Sub-Basin, West Sulawesi by (Sutadiwiria 2019). The availability of the data is presented inTable3. The lithostratigraphic analysis of the study area revealed that the samples were from the Middle Eocene Kalumpang Formation, which has an upper intertidal environment and comprises shale, as shown in Figure 4.

Table2
Maturity parameters of organic materials (Peters & Cassa1994)

Parameter	Maturity			Generation		
	Ro (%)	Tmax	TAI	Bit/TOC	Bitumen	PI
Immature	0.20 – 0.60	< 435	1.5 – 1.26	< 0.05	< 50	< 0.10
Early Mature	0.60 – 0.65	435 – 445	2.6 – 2.7	0.05 – 0.10	50 – 100	0.10 – 0.15
Peak Mature	0.65 – 0.90	445 – 450	2.7 – 2.9	0.15 – 0.25	150 – 250	0.25 – 0.40
Late Mature	0.90 – 1.35	450 – 470	2.9 – 3.3	-	-	> 0.40
Post Mature	> 1.35	> 470	> 3.3	-	-	-

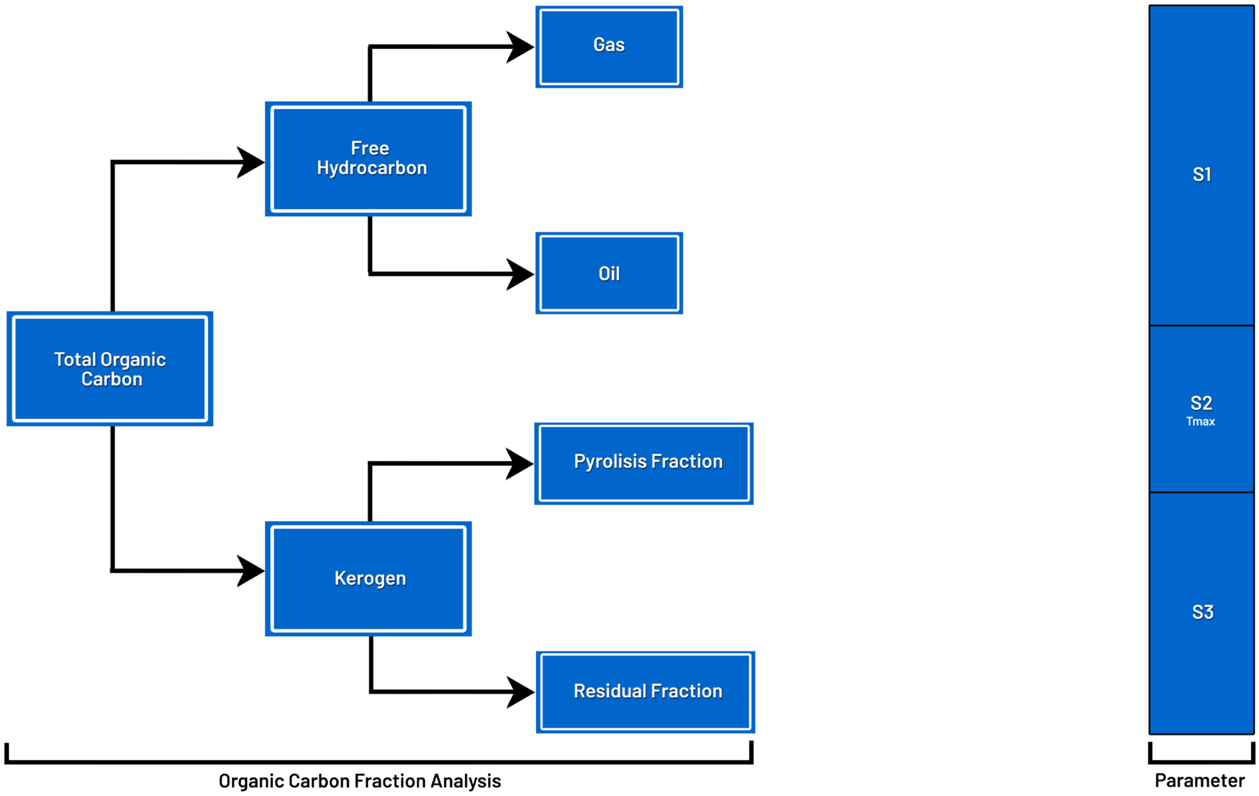

Figure 3
Methodology of rock-eval pyrolysis analysis (Soppanata 1996).

Table 3
Availability of data used in the research

	Sample Identification Name	Lithology	TOC	S1	S2	S3	Tmax	HI	OI	PI	VR (%)	Original References
Surface sample	**FS-12**	Shale	0.62	0.08	0.20	0.12	499	32	19	0.29	1.3	new data
	FS-2	Coal	30.56	0.61	33.29	21.01	423	109	69	0.02	0,46	Sutadiwiria et al. (2022)
	FS-20	Carbonaceous shale	6,92	0.28	11.94	2.58	429	189	37	0,02	0,38	Sutadiwiria et al. (2022)

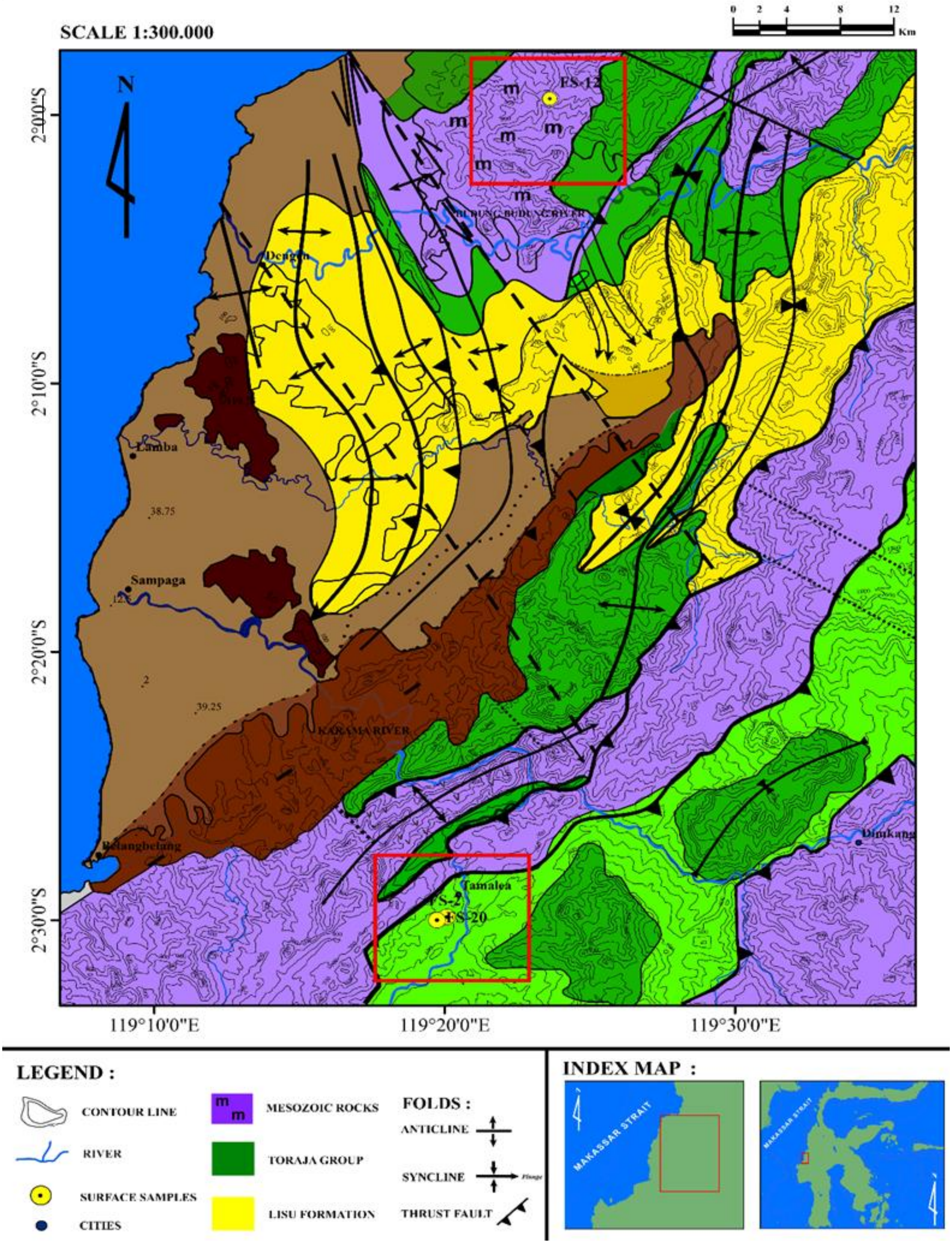

Figure 4
Location map and geology of Mamuju and surrounding areas modification of (Calvert & Hall 2003 and Raharjo et al.2012)

RESULT AND DISCUSSION

The analysis of the maturity level and type of hydrocarbon kerogen led to the conclusion that the FS-12 sample from the Mamuju area, West Sulawesi,belonged to the kerogen type IV (Figures 5 and 6). The hydrogen index (HI) value of the sample was found to be 32 (mg/grrock/% TOC, table, Figures 5and 6), which indicates that the kerogen has a lower potential to produce hydrocarbons as the HI value is less than the required 50 mg/gr rock (Waples 1985). More over, the tmax value of FS-12 was 499°C, which falls into the post-mature category based on (Peters & Cassa 1994), Figure 5 Previous studies on the surface samples (FS-2 and FS-20) showed high TOC values (30.56% and 6.32%, respectively) andHIvalues of 109 mg/C and 189 mg/C. Based on the HI value,the FS-2 and FS-20 samples were likely to have the potential to be gas-prone for FS-2 (type III kerogen), and to be oil and gas-prone for FS-20 (Type II kerogen) (modification of (Sutadiwiria et al. 2022) as shown in Table 3 and Figures 5 and 6.

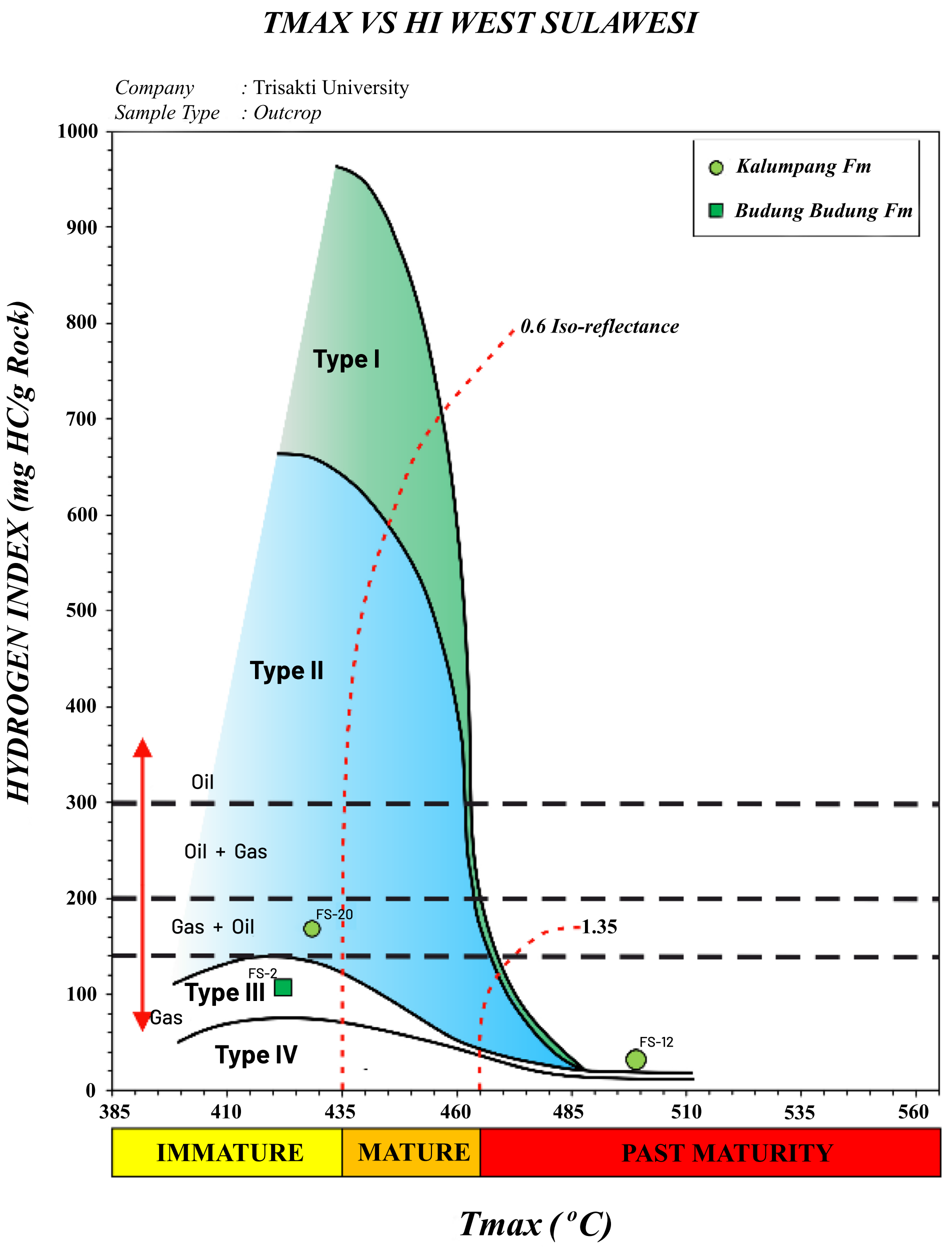

Figure 5
Results of crossplot diagram of hydrogen index (HI) vs Tmax of Mamuju West Sulawesi
(Van Krevelen 1993 & Waples 1985)

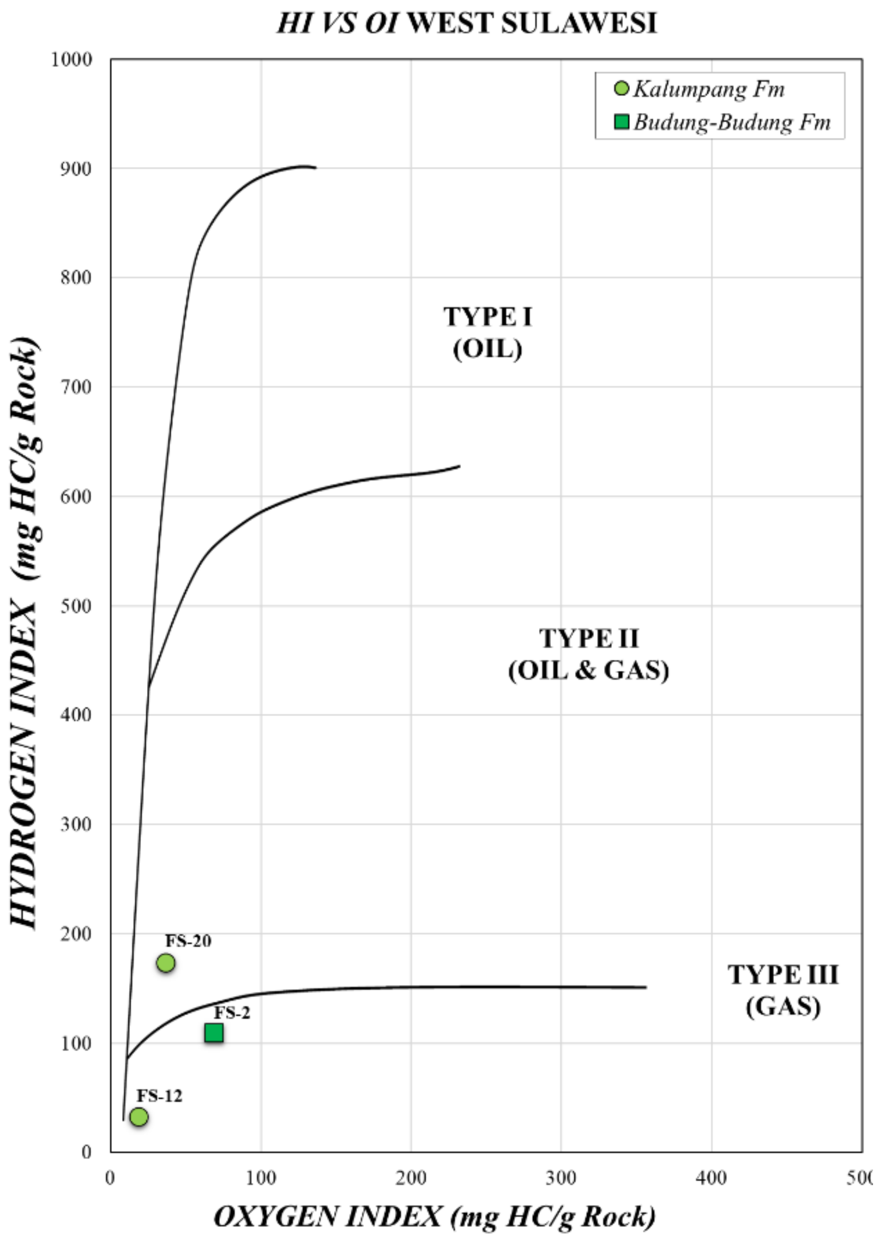

Figure 6
Results of crossplot diagram of van krevelen hydrogen index (HI) vs Oxygen Index (OI) Mamuju West Sulawesi (Van Krevelen 1993)

A number of terrestrial components (resin compounds), including the biomarkers oleanane (OL), bicadinane, and gamaserane (Gm), were visible in the mass fragmentogram profile, particularly the m/z 191 ion of the saturated hydrocarbon fraction of GCMS FS-12 (Figure 7). The se same biomarkers were also present in the samples FS-2 and FS-20 (Sutadiwiria et al. 2022) (Figures 8 and 9). The components W, T, and R originating from higher plants were identified as the bicadinane. These components were components a, b, c, and d. Ion taraxastana (Tx) also appeared in several samples along with the presence of oleanane. The ternary diagram ofsamples FS-2,FS-12, and FS-20 (Figure 10) from Peters et al. (2005) and Huang and Meinschein (1979) indicates a relative abundance plot of sterane (C27- C29), which shows a relatively high proportion of C29sterane. The percentages are 48.29%, 33.12%, and55.27%. In comparison C27 shows Figures of 26.5%, 36,69% and 10.73%, while C28 has percentages of 25.21%, 30.19% and 34%, respectively.

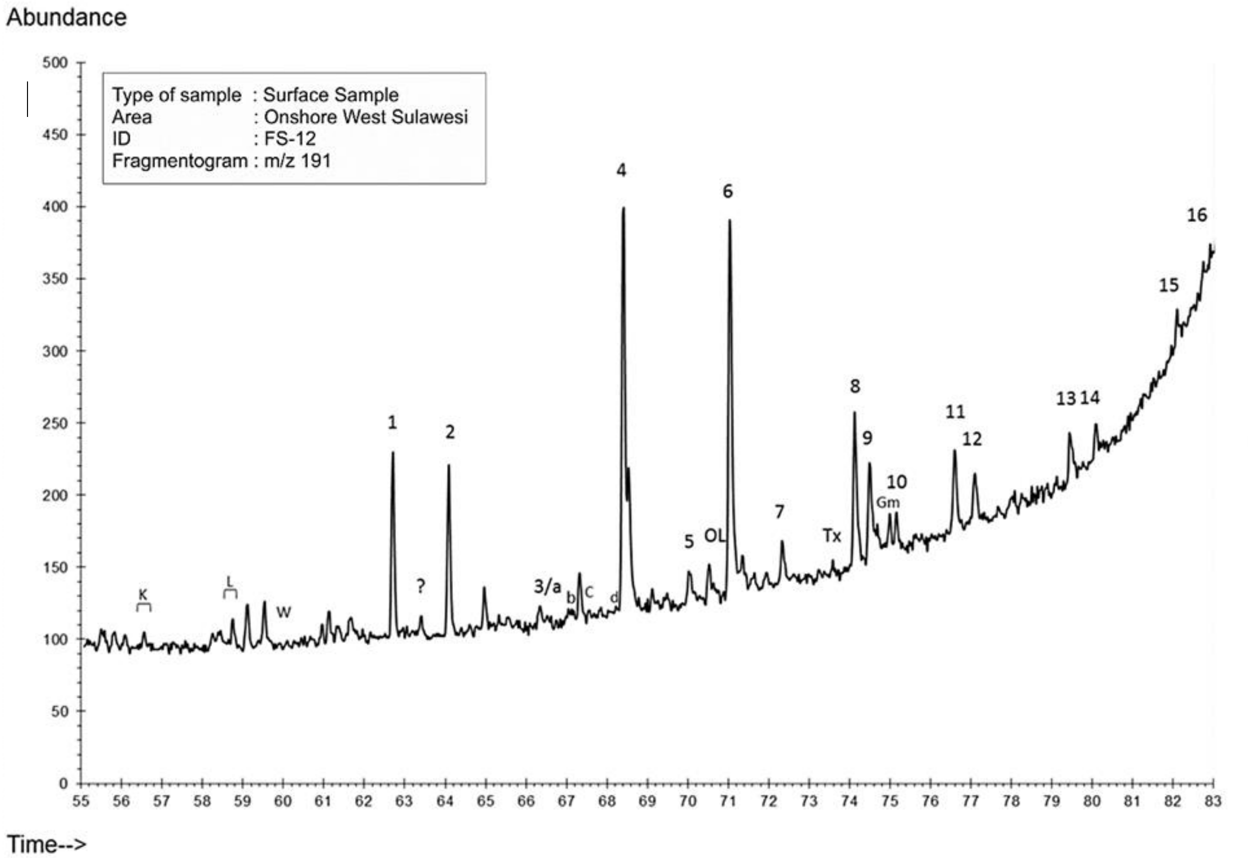

Figure 7
m/z 191 partial mass chromatograms showing triterpane distribution of FS-12

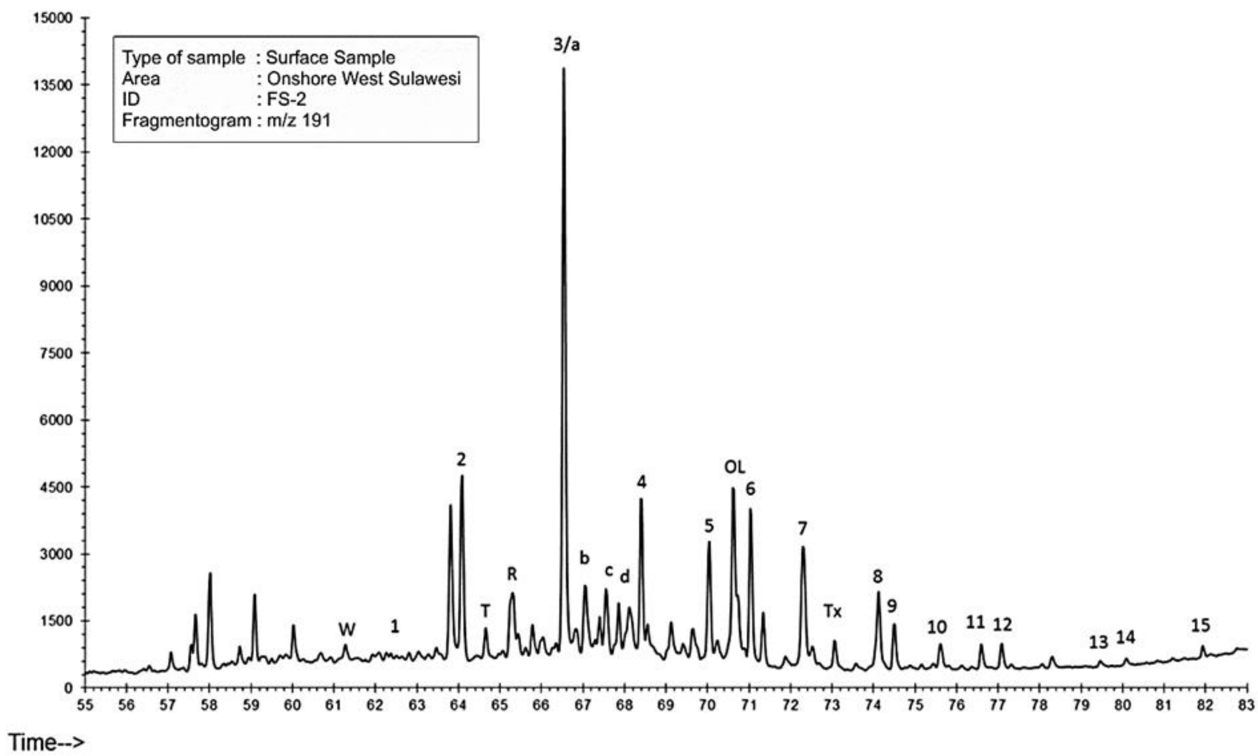

Figure 8
m/z 191 partial mass chromatograms showing triterpane distribution of FS-2. (Sutadiwiria et al. 2022)

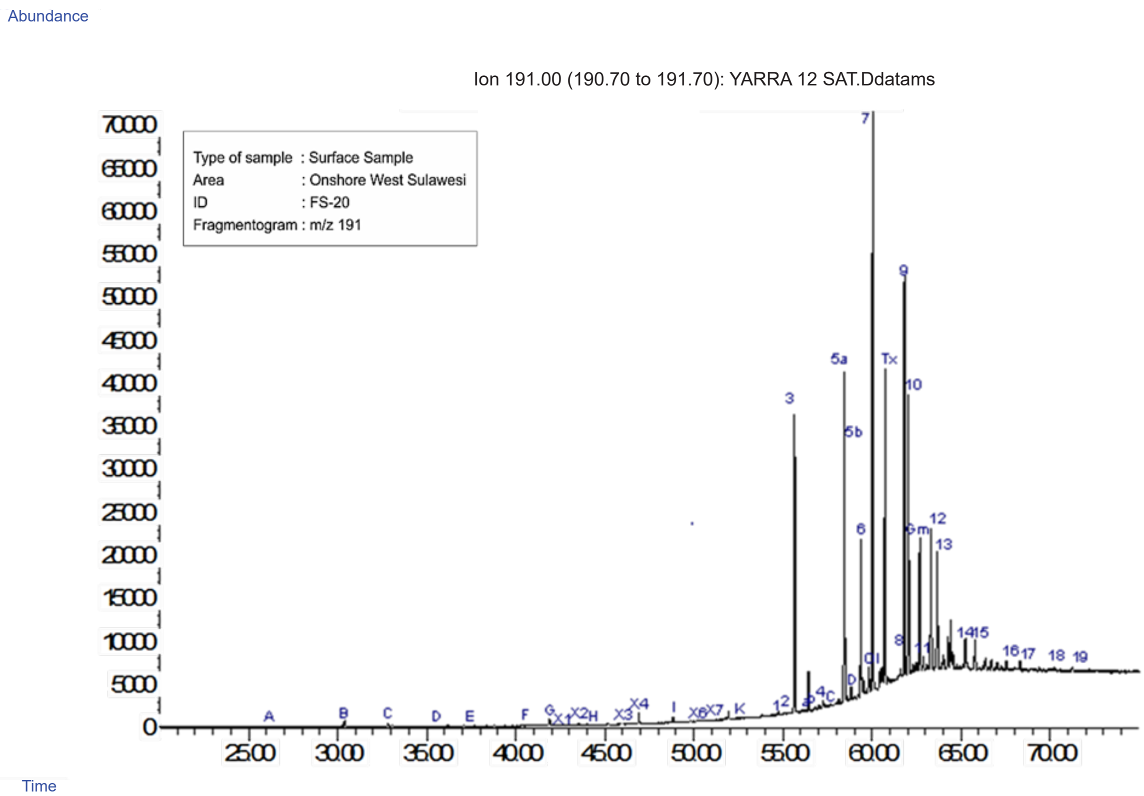

Figure 9
m/z 191 partial mass chromatograms showing triterpane distribution of FS-20 (Sutadiwiria et al. 2022)

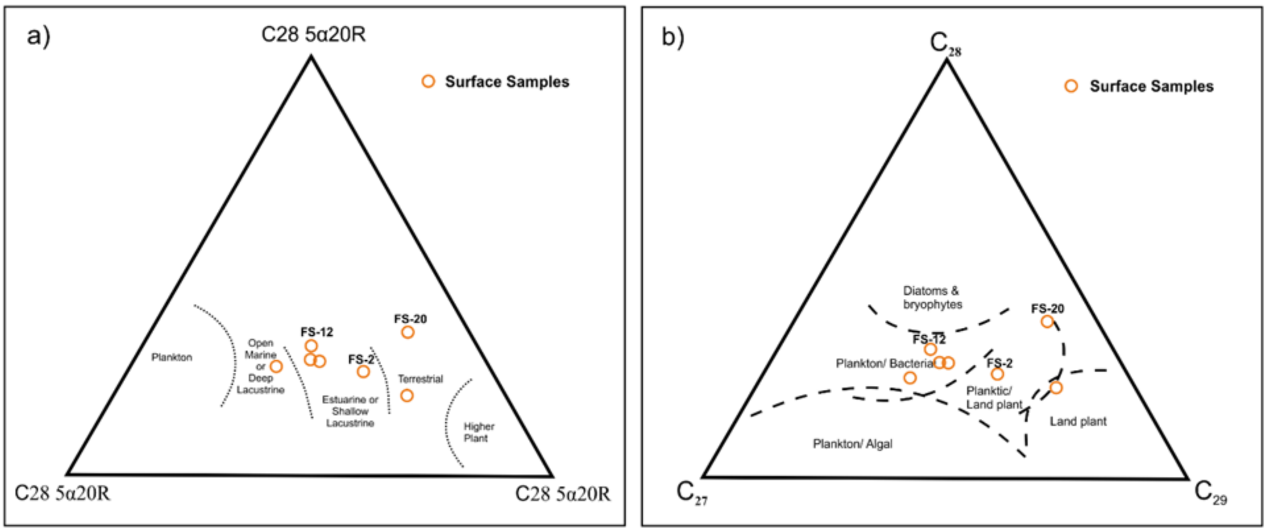

Figure 10
Saturated fraction of the surface sample extract plotted on the ternary diagram according to (a) (Huang & Meinschein 1979) and (b) (Peters et al. 2005)

The mass fragmentogram ion m/z 217 GCMS profile from samples FS-12, FS-02, and FS-20 further corroborates the ternary diagram (Figures 11, 12 and 13). This suggests that the three samples contain both terrestrial and marine organic materials. According to this update, organic materials derived from terrestrial and marine organic materials are deposited in the upper intertidal-fluviodeltaic environment as coal (FS-2), shale (FS-12), and carbonaceous shale (FS-20) (Sutadiwiria et al. 2022). This finding also accords with the study (Sutadiwiria et al. 2017) that found a significant amount of resin biomarkers in the source rock, indicating input from the fluviodeltaic environment.

Upon examination of the findings of the biostratigraphic, petrographic, and radiometric analyses of the current well K-1 in the eastern Makassar strait (Harsanti et al. 2013; Sutadiwiria et al. 2022), it becomes evident that the Late Cretaceous volcanic materials are located at a depth of 17,340–17,360 feet, while the shales and shale mudstones from the early paleocene and eocene are marginally lacustrine paleofacies (Geoservices 2012). The finding of lacustrine shale source rock in the eastern Makassar Strait was made possible by the comparatively higher concentration of C_{27} sterane in the well K-1 sample, when compared to C_{28} and C_{29} (Sutadiwiria et al. 2022).

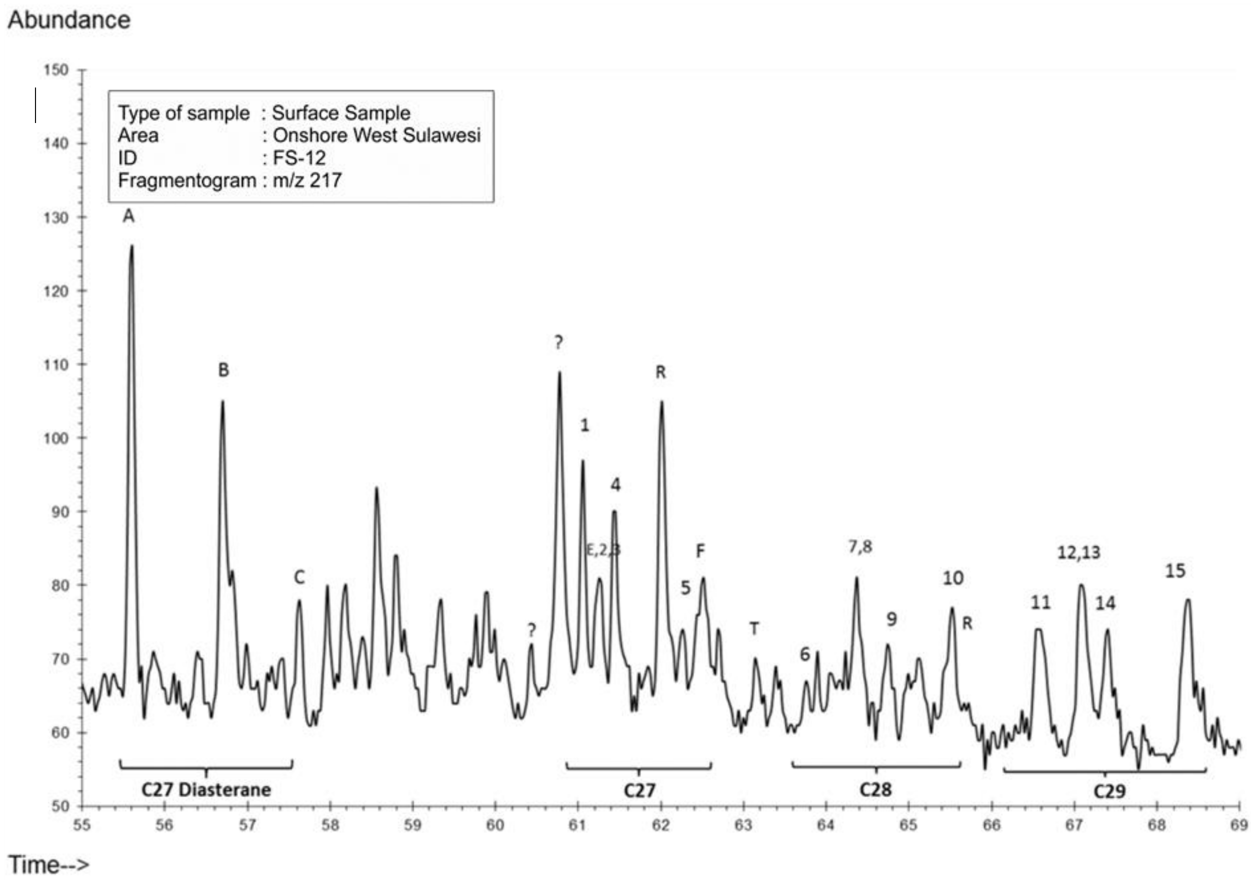

Figure 11
m/z 217 partial mass chromatograms showing sterane distribution of FS-12

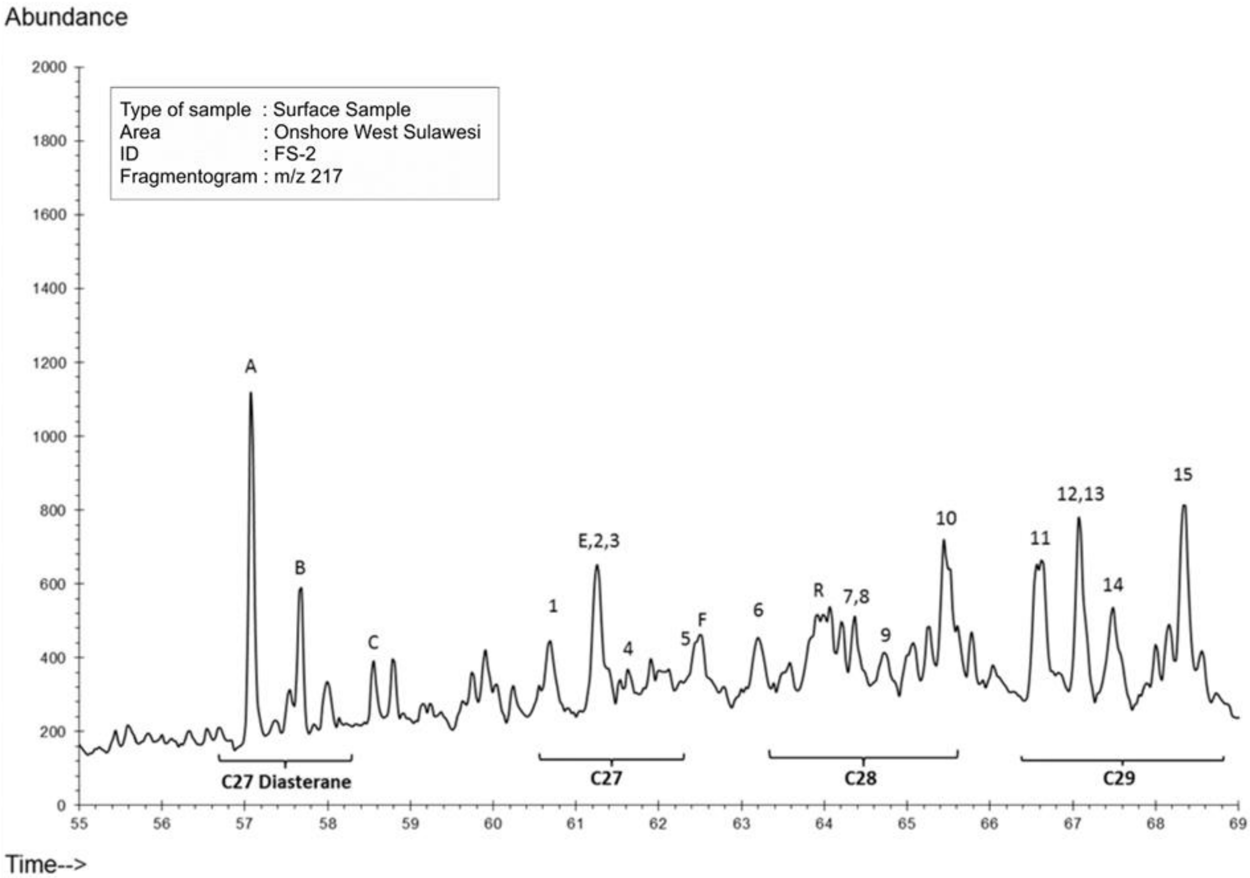

Figure 12
m/z 217 partial mass chromatograms showing sterane distribution of FS-2 (Sutadiwiria et al. 2022)

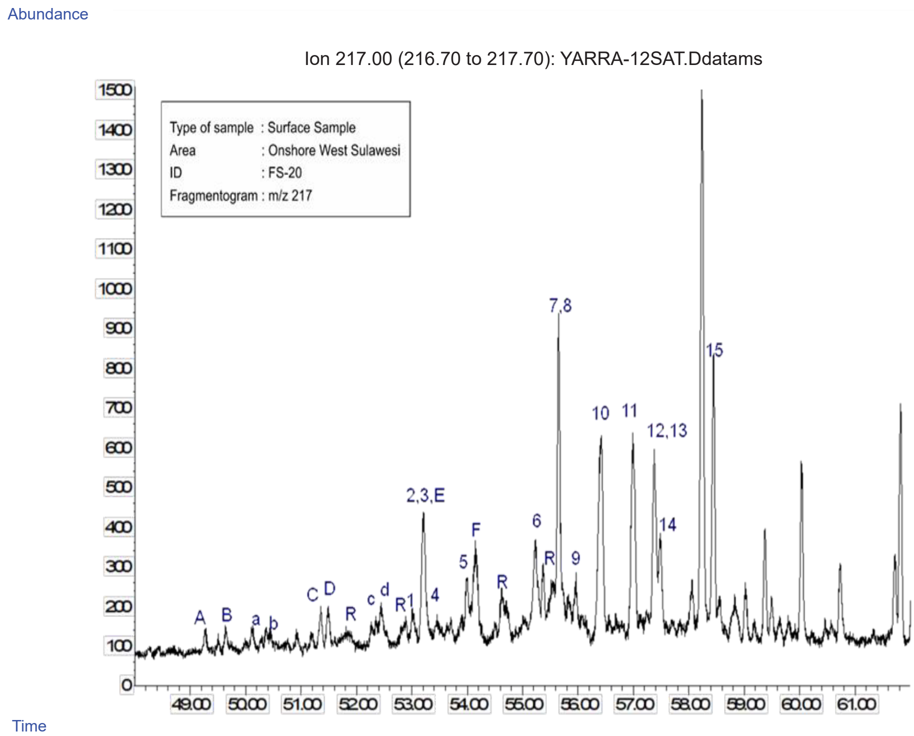

Figure 13
Modified m/z 217 partial mass chromatograms showing sterane distribution of FS-20 (Sutadiwiria et al. 2022)

CONCLUSION

After analyzing the hydrocarbons in the Lariang-Karama Sub-Basin, Mamuju, and West Sulawesi, it was found that the FS-12 sample from the Kalumpang formation had fair TOC content, but it was not a source rock in the study area due to its post-mature maturity level. The results indicate that it belongs to the Middle Eocene shale lithology and has no potential to become a source rock (Type IV), unlike FS-20 and FS-2, which displays potential for oil and gas generation (Types II and III kerogen, respectively). Following a thorough assessment of post-drilling laboratory study, the West Sulawesi area continues to hold potential to be explored, offering improved prospects and reduced risks for exploration activities in the region.

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GLOSSARY OF TERMS

Symbol	Definition	Unit
Tmax	Maximum Temperature	
TOC	Total Organic Carbon	
w.t%	Weight percent (of TOC)	
REP	Rock Eval Pyrolisis	
GC	Gass Chromatography	
GC-MS	Gass Chromatography and Mass Spectroscopy	
HI	Hydrogen Index	
OI	Oxygen Index	
PI	Production Index	
VR	Vitrinite Reflectance (Ro)	
S1	Free hydrocarbons	
S2	Pyrolisable hydrocarbon	
S3	Amount of CO_2 content present	
HI = mg/gr rock/% TOC	the amount of hydrogen relative to the amount of organic carbon present in a sample	
C	Carbon	
H	Hydrogen	
O	Oxygen	
N	Nitrogen	
S	Sulfur	
°C	Degrees Celsius	

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