Mining of Mineral Deposits
Volume 19 (2025), Issue 3, 43-50

MMD
JOURNAL / MINING.IN.UA

https://doi.org/10.33271/mining19.03.043

Application of inductively coupled plasma mass spectrometry for geochemical analysis of rocks to enhance oil and gas production forecasting

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Abstract

Purpose. This study aims to improve the accuracy of forecasting oil and gas deposits by analyzing the spatial distribution and dynamics of hydrocarbon gas concentrations within wells using inductively coupled plasma mass spectrometry (ICP-MS).

Methods. Core samples were collected from various regions of Azerbaijan. The samples underwent microwave mineralization and were analyzed using the quadrupole mass spectrometer Agilent ICP-MS 7700e. The study of gas composition and mineralogical characteristics of rocks considered factors influencing hydrocarbon migration, including pH environment, redox potential, temperature, and pressure.

Findings. It was established that hydrocarbon gas concentrations increase in depth due to the presence of oil and gas reservoirs and under the influence of geochemical zoning. It was shown that the migration of hydrocarbons and trace elements affects the mineralogical composition of rocks. The analysis of the elemental composition of cores helped reduce the number of unproductive wells from 70% to 30%, leading to a 10% reduction in exploration costs.

Originality. The novelty of this study lies in integrating lithochemical analysis with highly sensitive geochemical methods, such as ICP-MS, to examine the composition and properties of rocks in detail. For the first time, a correlation between geochemical anomalies and hydrocarbon migration zones has been identified for oil and gas fields in Azerbaijan.

Practical implications. The research findings can be used to optimize geological exploration and improve the accuracy of oil and gas field forecasting. The methodology can be adapted for regions with similar geological conditions, enhancing exploration efficiency and reducing costs.

Keywords: *oil and gas fields, inductively coupled plasma mass spectrometry, geochemical method, hydrocarbon migration, exploration well*

1. Introduction

Geochemical methods are fundamental in modern oil and gas exploration, contributing significantly to theoretical understanding and practical implementation of prospecting activities. The rapid depletion of easily accessible oil and gas reserves, increasing global energy demands, and the transition towards sustainable energy systems necessitate adopting advanced exploration techniques. These techniques must ensure greater accuracy in identifying hydrocarbon-bearing formations while minimizing exploration costs. Azerbaijan, possessing a long-standing history of oil production, faces challenges in exploring new deposits, particularly in geologically complex regions. This underlines the need for sensitive analytical methods to provide more reliable insights into subsurface compositions and hydrocarbon migration pathways.

In the last two decades, considerable progress has been made globally in applying geochemical methods to hydrocarbon exploration. Studies by Ken and Martin (2002), Lawson et al. (2022), and Balaram (1996) highlight how geochemistry has evolved from simple surface sampling to complex instrumental techniques such as mass spectrometry [1]-[3] In Azerbaijan, research has traditionally focused on geological mapping and stratigraphic analysis [4], [5], with some introduction of geochemical techniques since the 2000s. Despite these advancements, existing methods often lack the sensitivity and resolution to detect subtle geochemical anomalies, particularly in areas with intricate lithological structures. Furthermore, limited geochemical and lithological data integration has restricted the predictive accuracy of hydrocarbon exploration models.

A critical review of recent publications reveals a growing trend in utilizing direct geochemical prospecting methods, especially those involving the detailed analysis of hydrocarbon composition and spatial distribution. For instance, Lei et

Received: 25 October 2024. Accepted: 28 July 2025. Available online: 30 September 2025

Mining of Mineral Deposits. ISSN 2415-3443 (Online) | ISSN 2415-3435 (Print)

al. (2024) and Munoz-Lopez et al. (2022) have demonstrated the utility of high-resolution mass spectrometry techniques in identifying hydrocarbon generation zones and migration pathways [6], [7]. However, these studies have primarily focused on large sedimentary basins outside the Caspian region, leaving a notable gap in understanding the unique geochemical signatures of the South Caspian Basin and Azerbaijani deposits.

The unresolved aspects of current research are the limited application of highly sensitive inductively coupled plasma mass spectrometry (ICP-MS) in hydrocarbon prospecting within Azerbaijan. Most studies have concentrated on organic geochemistry, overlooking the valuable information embedded in the inorganic elemental composition of rocks [8]. Additionally, the absence of comprehensive studies correlating trace elemental distribution with hydrocarbon migration zones has hindered the development of more accurate predictive models for exploration drilling. Furthermore, prior research has not sufficiently addressed how geochemical zoning influences the distribution of productive and non-productive wells. It has not systematically explored the influence of depth-dependent elemental variations on reservoir quality [9], [10].

This paper addresses these gaps by applying ICP-MS for the detailed geochemical analysis of core samples collected from various Azerbaijani oil and gas deposits. The study seeks to elucidate the relationship between trace element concentrations and hydrocarbon migration, offering a novel approach to reducing the number of unproductive wells and enhancing the efficiency of exploration activities. By establishing clear correlations between geochemical anomalies and hydrocarbon-bearing zones, the research intends to refine geological models used in the oil and gas industry [11], [12].

To achieve this aim, the following research objectives have been formulated:

– to conduct a comprehensive literature review on the application of geochemical methods, particularly ICP-MS, in oil and gas exploration;

– to analyze core samples from selected Azerbaijani deposits using ICP-MS, focusing on depth-dependent variations in elemental concentrations;

– to identify and map geochemical anomalies associated with hydrocarbon migration pathways;

– to investigate the influence of key factors such as pH, redox potential, and fluid dynamics on elemental distributions;

– to evaluate the practical impact of geochemical data on reducing unproductive drilling and optimizing exploration costs;

– to develop a methodological framework for applying ICP-MS in future geological explorations in Azerbaijan and similar geological settings.

By implementing these objectives, this study aims to advance the geochemical understanding of Azerbaijani oil and gas fields and contribute to developing more accurate and cost-effective exploration strategies. The findings will provide a valuable reference for national and international researchers and practitioners engaged in hydrocarbon exploration [13], [14].

2. Methods

The study was conducted using core samples provided by the AzLab laboratory of SOCAR. The samples were collected from various regions of Azerbaijan, including Western Absheron, Pirallahi, Jilov, Buzovna-Mashtaga, and Gunashli. Figure 1 presents the geographical locations of the studied deposits (or sites) on the Absheron Peninsula. The coordinates of the key points, including Buzovna-Mashtaga, Pirallahi, Western Absheron, Gunashli, and Jilov, are marked with red indicators. This graph illustrates the distribution of the deposits (or sites) according to their latitude and longitude, allowing for a visual assessment of their geographical positioning.

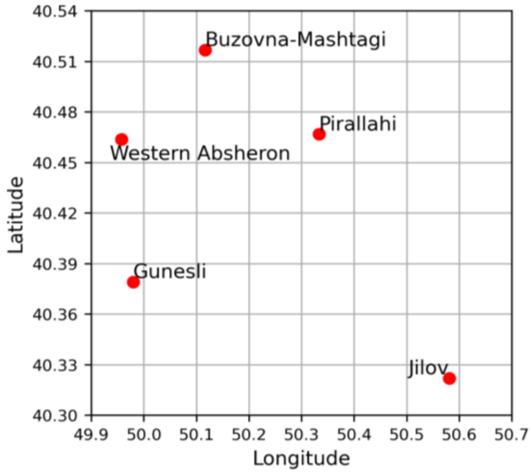

Figure 1. Geographical location of the studied deposits (or sites) on the Absheron Peninsula

Table 1 provides data on depths (in meters) for various regions, including Western Absheron, Pirallahi, Jilov, Buzovna-Mashtaga, and Gunashli. Depth values are given for ten levels, enabling the tracking of parameter variations with increasing well depth at each studied deposit [15].

Table 1. Core samples from various regions of Azerbaijan

Area	Western Absheron	Pirallahi	Jilov	Buzovna-Mashtaga	Gunashli
No.	Depth (m)				
1	187.0	104.4	264.2	238.9	100.0
2	420.5	571.0	500.0	676.0	404.0
3	765.6	973.9	893.5	1080.5	800.1
4	1005.0	1312.6	1127.1	1424.1	1231.6
5	1300.0	1707.0	1410.0	1834.5	1511.0
6	1631.0	2132.0	1735.2	2209.0	1836.0
7	1933.5	2540.5	2060.0	2644.0	2170.5
8	2276.5	2992.0	2315.0	3007.5	2417.0
9	2530.2	3340.2	2710.0	3400.0	2921.0
10	2829.0	3653.5	3030.0	3721.7	3340.0

Sample mineralization was carried out using the Speedwave Xpert microwave digestion system (Germany), which ensures precise temperature control and is equipped with small-volume vessels designed for working with microsuspensions. The microwave digestion methods are presented in Tables 2 and 3. The analysis of the samples was performed using a quadrupole inductively coupled plasma mass spectrometer (ICP-MS 7700e) manufactured by Agilent Technologies (USA) (Fig. 2) [16]-[18].

The following gases, reagents, and solutions were used in the study:

– gases (argon and helium);

– acids: high-purity nitric acid (65% “for analysis”, Merck, Germany), hydrochloric acid (35%, Merck, Germany), and hydrogen peroxide (H_2O_2 – 30% Suprapur, Merck, Germany).

Table 2. Microwave treatment of core samples

Reagents	Acid			Volume		
	HNO_3 (65%)			10 mL		
Procedure	Weigh 3.5-4.0 g of the sample into the digestion vessel, ensuring that the amount of organic material does not exceed 250 mg. Add 10 mL of HNO_3 to the boat. Gently shake or stir the mixture with a clean Teflon or glass stirrer. Allow the mixture to sit for at least 10 minutes before sealing the vessel. Heat the vessel in the microwave using the following program:					
Temperature program	Step	*T*, °C	*P*, bar	Ta, min	Time, min	Power, %
	1	175	30	5	5	90
	2	50	25	1	10	0

Table 3. Microwave treatment of core samples

Reagents	Acid			Volume		
	HNO_3 (65%)			2.5 mL		
	HCI (37%)			7.5 mL		
Procedure	Weigh 0.5-1.0 g of the sample into the digestion vessel, ensuring that the amount of organic material does not exceed 250 mg. Add 2.5 mL of HNO_3 and 7.5 mL of HCl to the boat. Gently shake or stir the mixture with a clean Teflon or glass stirrer. Wait at least 10 minutes before sealing the vessel. Then, heat the boat in the microwave according to the following program:					
Temperature program	Step	*T*, °C	*P*, bar	Ta, min	Time, min	Power, %
	1	180	30	2	25	90
	2	50	25	1	10	0

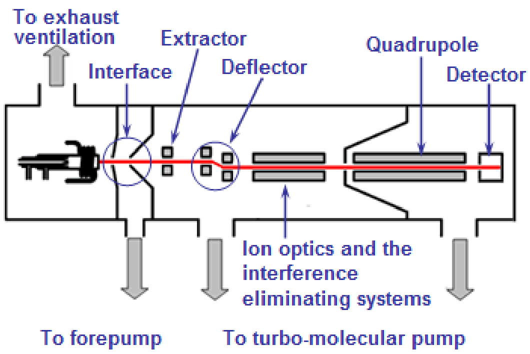

Figure 2. Diagram of the ICP-MS Agilent 7700e

The ICP-MS Agilent 7700e system operates through several essential components that facilitate detecting and quantifying trace elements in geological samples. A nebulizer introduces samples in liquid form, which converts the liquid into a fine aerosol. The aerosol is carried by argon gas into the plasma torch.

A high-frequency radio wave generates plasma with temperatures reaching approximately 6000-10000 K. Within this plasma, the elements in the sample are ionized, forming positively charged ions. The ions then pass through the sampler and skimmer interface cones, reducing the pressure from atmospheric levels in the plasma to the vacuum conditions required for the mass spectrometer.

The ion optics system focuses the ion beam, eliminates neutral particles, and directs the positively charged ions toward the mass analyzer. This stage helps minimize interferences and ensures accurate ion transmission. The quadrupole filters ions according to their mass-to-charge (m/z) ratio by applying oscillating electric fields. Only ions with specific m/z values pass through to the detector, enabling precise elemental separation.

A collision/reaction cell with helium or other gases may be used to remove polyatomic interferences, thereby improving measurement accuracy. Finally, the detector, typically an electron multiplier, counts the ions and converts the resulting signals into quantitative data for analysis.

Thus, ions are formed in the high-temperature plasma, transported through the interface region under vacuum, filtered by the quadrupole according to their mass-to-charge ratio, and finally detected to quantify elemental concentrations. This multi-stage process ensures high sensitivity, low detection limits, and accurate determination of trace elements in geological samples, essential for practical geochemical analysis and hydrocarbon prospecting [16]-[18].

3. Results and discussion

Figures 3-7 present the elemental composition of core samples collected from various depths of deposits in specific regions of Azerbaijan.

According to Figure 3, core samples from the Western Absheron region at depths of 187.0, 765.6, 1300.0, 1933.5, and 2829.0 meters contain elements such as Mg, Cu, Zn, Sr, and In. Their concentration increases with depth, indicating hydrocarbon migration processes in this zone. This increase in concentration suggests the potential oil and gas-bearing capacity of the reservoir at these depths.

Figure 4 shows an increase in the concentration of Al and Fe in samples taken from the Pirallahi region. The variation in their content with depth may indicate geochemical processes occurring within the deposit. The high concentration of Al and Fe in deeper layers highlights their significance for assessing the geological characteristics of this area.

Figure 5 shows a high concentration of Mn in the Jilov area at depths of 500.0-1127.0 m. This may indicate an increased potential for detecting Mn in layers at 2060-3030 m depths. Indeed, at a depth of 2000 m, the concentration of Mn doubles. The observed correlation between depth and Mn content highlights the importance of studying this element in geochemical research.

Figure 6 shows a low Zn concentration at depths of 1834.5-2644.0 m in the Buzovna-Mashtaga area, whereas zinc is not detected at shallower depths, such as 238.90 m. However, its content sharply increases at 2644.0-3721.0 m intervals. While the presence of Zn at these depths may improve oil and gas field forecasting, its low concentration in deeper layers indicates a low probability of detection in near-surface horizons (100-1000 m). This suggests possible limitations in predicting reservoirs based on Zn data.

Figure 7 shows the presence of Ca in core samples taken from the Guneshli area at depths of 2170-3340 m. As depth increases, its concentration rises, which may indicate specific conditions for hydrocarbon formation and migration. Additionally, a small amount of Sr is detected in the upper layers (100-800 m); however, at depths exceeding 1000 m, its concentration sharply decreases until it disappears completely.

As seen in Figures 3-7, the elemental composition of core samples varies with depth, reflecting the influence of geochemical processes and hydrocarbon migration. Each studied area is characterized by a unique element distribution, determined by geological conditions.

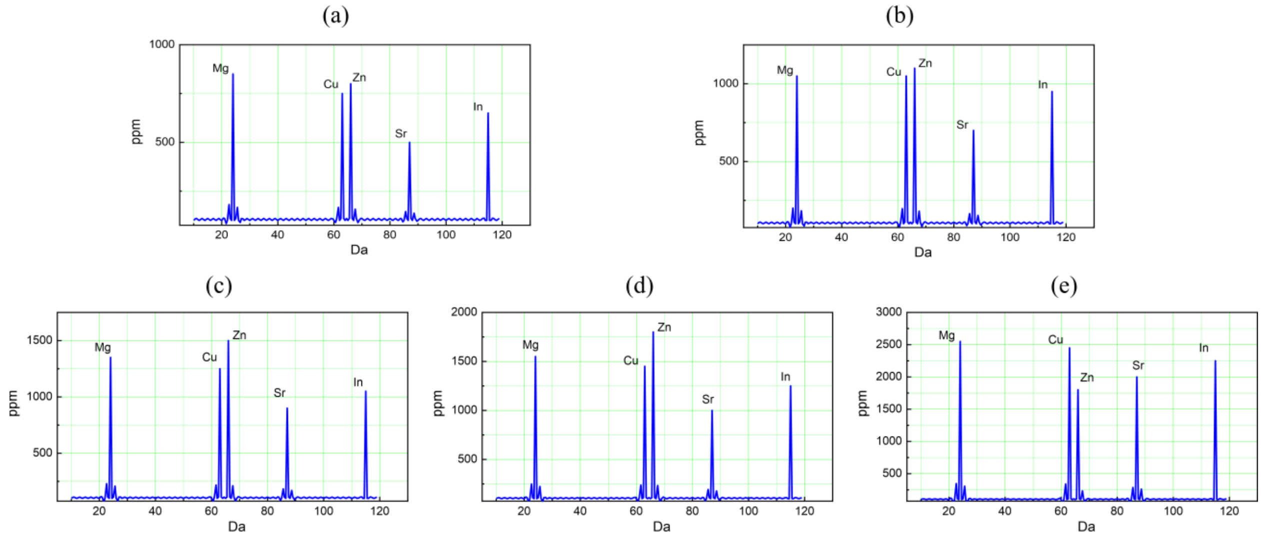

Figure 3. Elemental composition of core samples taken at various depths in the Western Absheron area: (a), (b) upper layer (depths 187.0-420.5 m); (c), (d) middle layer (depths 1005.0-1300.0 m); (e) – lower layer (depths 2276.5-2829.0 m)

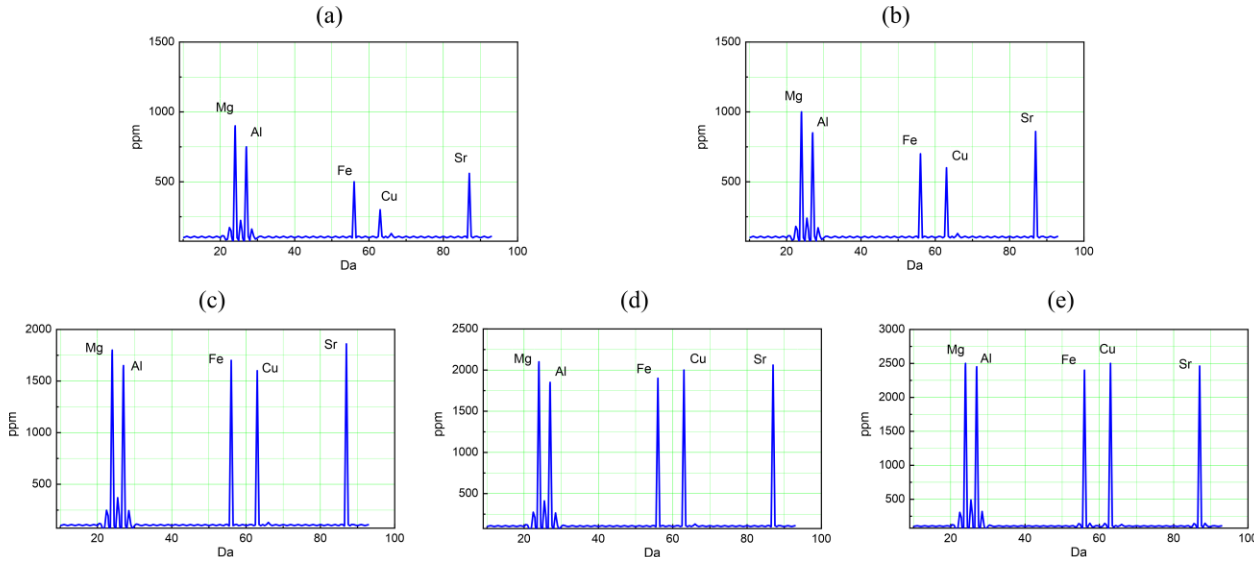

Figure 4. Elemental composition of core samples taken at various depths of the Pirallahi field: (a), (b) upper layer (depths 104.4 = -571.0 m); (c), (d) middle layer (depths 1707.0-2132.0 m); (e) lower layer (depths 2992.0-3653.5 m)

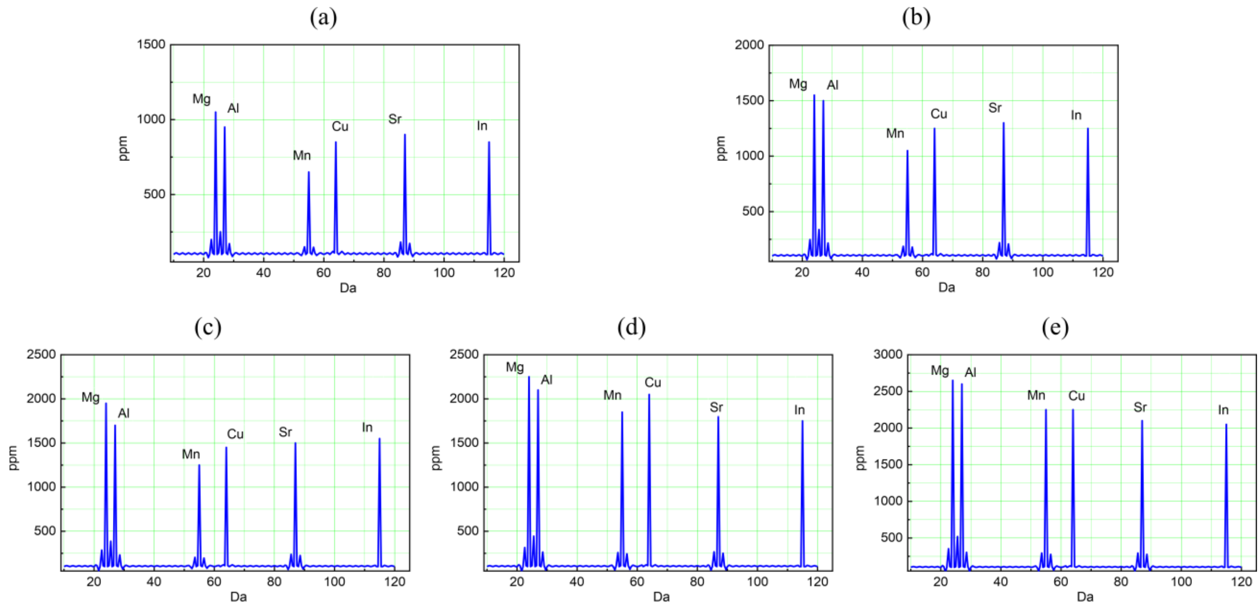

Figure 5. Elemental composition of core samples taken at various depths in the Jilov area: (a), (b) upper layer (depths 264.2-893.5 m); (c), (d) middle layer (depths 1410.0-1735.2 m); (e) lower layer (depths 2315.0-3030.0 m)

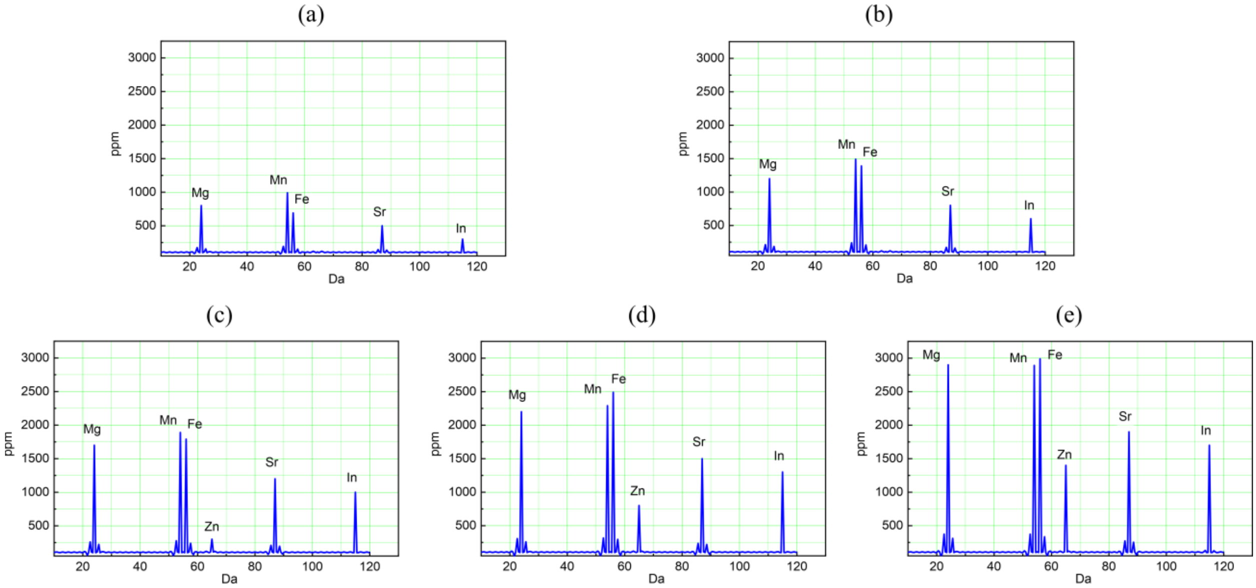

Figure 6. Elemental composition of core samples taken at various depths in the Buzovna-Mashtaga area: (a), (b) upper layer (depths 238.9-676.0 m); (c), (d) middle layer (depths 1424.1-1834.5 m); (e) lower layer (depths 2644.0-3400.0 m)

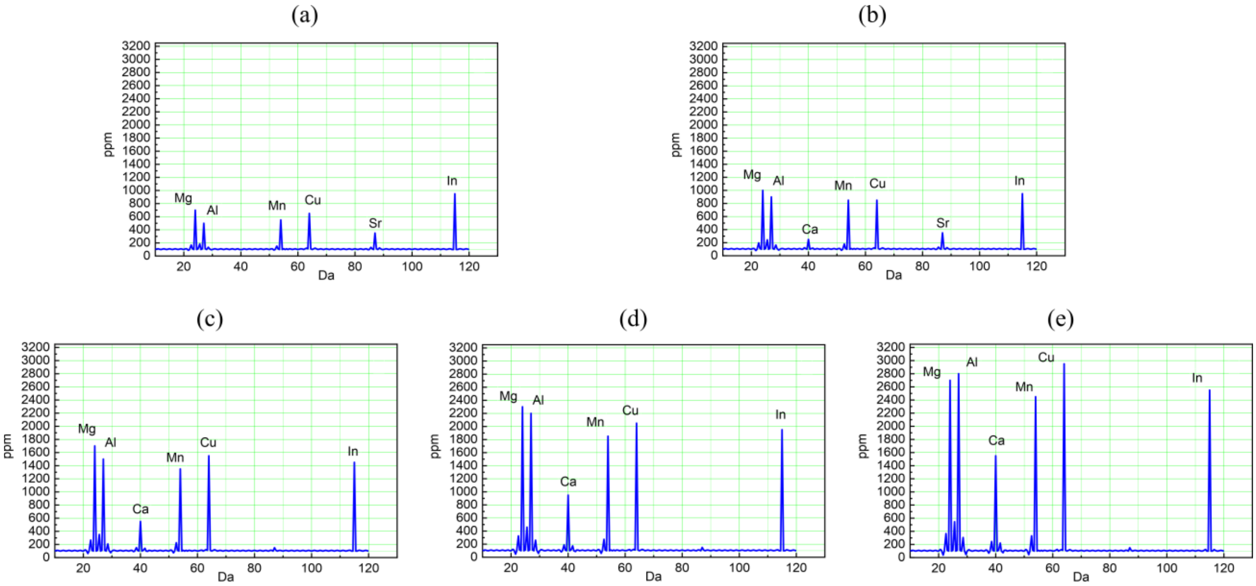

Figure 7. Elemental composition of core samples taken at various depths in the Guneshli area: (a, (b) upper layer (depths 100.0-404.0 m); (c), (d) middle layer (depths 1231.6-1511.0 m); (e) lower layer (depths 2417.0-3340.0 m)

The analysis of cores from different regions shows significant variations in the content of key elements, which may be associated with hydrocarbon migration, the geochemical properties of rocks, and their formation conditions. The obtained data contribute to refining geological models and predicting hydrocarbon-bearing zones.

In addition to analyzing the elemental composition of rocks, the Mg/Al and Fe/Cu ratios in solid rocks at various well depths were calculated (Fig. 8). Changes in these ratios allowed for the construction of element distribution maps along the cross-section and across the study area. Taken together, these data help identify fluid migration zones from hydrocarbon reservoirs, providing additional information for assessing the prospects of exploration sites.

Figure 8 shows that solid rock element concentration ratios (Mg/Al, Fe/Cu) consistently vary with drilling depth.

The observed trends may indicate zones with increased or decreased concentrations of certain elements, which are associated with geochemical processes in the rocks.

Changes in the ratios, especially within specific depth intervals, may suggest the presence of fluid migration pathways from oil and gas reservoirs. For example, anomalous Fe/Cu or Mg/Al values may mark areas where rock interaction with hydrocarbon systems has occurred. In zones with limited gas exchange, the composition of rocks undergoes significant changes under the influence of penetrating aqueous solutions and gases. These transformations play a key role in the formation of the reservoir properties of rocks.

The primary mechanism of these changes is related to the dolomitization process, in which magnesium ions replace calcium in the crystalline lattice of carbonate minerals. This substitution enhances the filtration and reservoir properties of the rocks, creating favorable conditions for hydrocarbon accumulation. It is imperative to note that an increase in rock mass porosity often accompanies this process. Carbon dioxide plays a crucial role in rock transformation. Its concentration directly affects the carbonate equilibrium in the system [19], [20]:

$$Ca(HCO_3)_2 \rightleftarrows CaCO_3 + CO_2 + H_2O.$$

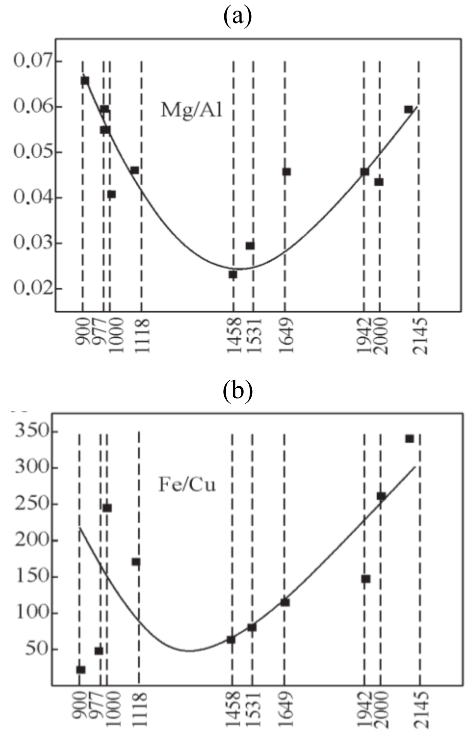

Figure 8. Ratio of element concentrations in rock composition: (a) Mg/Al; (b) Fe/Cu

At high CO_2 concentrations, the equilibrium shifts toward forming soluble bicarbonates, reducing the acidity of the environment. Conversely, a decrease in carbon dioxide concentration promotes the precipitation of carbonate deposits.

Several key factors significantly influence mineral formation processes:

– temperature conditions;

– the degree of water mineralization;

– magnesium-to-calcium ion concentration ratios;

– characteristics of the hydrodynamic regime.

It should be emphasized that rock transformation occurs under the combined influence of these factors. For example, dolomitization processes can become significantly more active under certain temperature conditions and a specific ionic composition of the aqueous environment.

The studies convincingly demonstrate the crucial role of gas components in rock formation processes. However, to obtain a complete picture, it is necessary to consider the full range of factors from the mineral composition of the original rocks to the specifics of fluid migration under reservoir conditions. Data analysis across various depth intervals reveals a clear correlation between thermobaric conditions and the development of reservoir properties in rocks.

Due to tectonic processes occurring after the formation of deposits, migration pathways for fluids develop over geological time. Deep, highly mineralized waters, carrying dissolved and free hydrocarbons through these pathways, migrate toward the upper horizons. These waters are typically enriched with elements such as Mg, I, Cu, Zn, Br, Pb, Th, and V and contain CO_2, and in some cases, H_2S.

In the zone of restricted gas exchange, intense Fe^+ and Mn^+ ion leaching, increased rock radioactivity, and loosening of clays and limestones are observed. These changes lead to a decrease in the electrical resistivity of the rocks. In this hydrodynamic zone, the interaction of hydrocarbons with rocks results in the formation of CO_2 and various organo-mineral complexes, some of which migrate into the upper geochemical zone. As a result, the concentrations of key rock-forming elements such as Ca, Si, Mg, Na, K, Fe, and others change.

Thus, alterations in the elemental and mineral composition of rocks are recorded in geochemical zones where fluids migrate from oil and gas reservoirs. This study observes specific changes, such as increased dolomitized minerals and shifts in the calcium-to-magnesium carbonate ratio, caused by ion exchange and dissolution processes under the influence of migrating fluids. These changes are confirmed by chemical and mineralogical analyses of samples from various depths, indicating the significant impact of fluids on the composition and physical properties of the rocks.

The conducted experiments indicate that while all the studied deposits are rich in common elements such as Mg, Mn, Al, Cu, and In, some areas also show very low concentrations of Zn, Fe, and Ca. The analysis revealed that the concentration of all elements increases with depth, confirming a significant dolomitization process in these core samples.

A comprehensive approach has been applied for the first time in Azerbaijani deposits, combining inductively coupled plasma mass spectrometry (ICP-MS) with traditional geochemical methods. This approach enabled the detailed mapping of element distribution (Mg, Al, Fe, Cu, Zn, Sr, In, etc.) across well depths. It established a correlation between geochemical anomalies and hydrocarbon migration zones.

The elemental analysis of core samples demonstrated that the observed geochemical profiles allowed for a reduction in the number of unproductive wells: out of 10 drilled wells, 3 were productive, leading to a 10% decrease in exploration costs.

Mass spectrometric data for core analysis significantly improves hydrocarbon prospecting, as evidenced by resource savings and increased exploration efficiency. This opens new opportunities for applying similar methodologies in regions with complex geological conditions.

4. Conclusions

The application of inductively coupled plasma mass spectrometry (ICP-MS) for analyzing core samples from various depths of Azerbaijani deposits has revealed patterns in the distribution of elements (Mg, Al, Fe, Cu, Zn, Sr, In) that correlate with hydrocarbon migration zones. It has been established that the concentrations of these elements increase with depth, which is associated with dolomitization processes and the improvement of reservoir properties in rocks.

The results demonstrate that geochemical anomalies, such as elevated Mg/Al and Fe/Cu ratios, are reliable indicators of hydrocarbon-bearing formations. Well productivity data prove this: this method reduced unproductive wells from 70% to 30%, leading to a 10% decrease in exploration costs.

The study also highlighted the influence of carbon dioxide and other fluids on carbonate equilibrium and the mineralogical composition of rocks. The observed changes, including increased porosity and dolomitization, confirm the significant role of fluid dynamics in reservoir formation.

The data obtained emphasizes the effectiveness of ICP-MS for hydrocarbon prospecting and the optimization of geological exploration. This methodology can be adapted for other regions with complex geological conditions, opening new prospects for hydrocarbon exploration.

Author contributions

Conceptualization: TN, AH; Data curation: TN; Formal analysis: NI; Funding acquisition: TN, KN; Investigation: TN; Methodology: TN; Resources: TN; Software: NI; Supervision: KN; Validation: AH; Visualization: TN, ZN; Writing – original draft: TN; Writing – review & editing: ZN, KN. All authors have read and agreed to the published version of the manuscript.

Funding

The authors express their deep gratitude to SOCAR Scientific Foundation of the State Oil Company of the Azerbaijan Republic for the financial support provided under grants No. 01 LR – AMEA 04.01.2018 and No. 10 LR – AMEA 07.01.2024.

Conflicts of interest

The authors declare no conflict of interest.

Data availability statement

The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

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Застосування мас-спектрометрії з індуктивно-зв’язаною плазмою для геохімічного аналізу гірських порід з метою покращення прогнозування видобутку нафти і газу

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Мета. Підвищення точності прогнозування родовищ нафти і газу шляхом аналізу просторового розподілу та динаміки концентрацій вуглеводневого газу в свердловинах за допомогою методу мас-спектрометрії з індуктивно-зв’язаною плазмою.

Методика. Кернові зразки були відібрані з різних регіонів Азербайджану. Зразки пройшли мікрохвильову мінералізацію та були проаналізовані за допомогою квадрупольного мас-спектрометра Agilent ICP-MS 7700e. При вивченні газового складу та мінералогічних характеристик порід розглядалися фактори, що впливають на міграцію вуглеводнів, включаючи pH середовища, окисльовально-відновний потенціал, температуру та тиск.

Результати. Встановлено, що концентрації вуглеводневого газу збільшуються з глибиною через наявність нафтогазових покладів та під впливом геохімічного районування. Доведено, що міграція вуглеводнів та мікроелементів впливає на мінералогічний склад гірських порід. Аналіз елементного складу кернів допоміг зменшити кількість непродуктивних свердловин з 70 до 30%, що призвело до зниження витрат на розвідку на 10%.

Наукова новизна. Новизна дослідження полягає в інтеграції літохімічного аналізу з високочутливими геохімічними методами, такими як ІСП-МС, для детального вивчення складу і властивостей гірських порід. Вперше було виявлено кореляцію між геохімічними аномаліями та зонами міграції вуглеводнів на нафтогазових родовищах Азербайджану.

Практична значимість. Результати дослідження можуть бути використані для оптимізації геологорозвідувальних робіт та підвищення точності прогнозування нафтогазових родовищ. Методологія може бути адаптована для регіонів зі схожими геологічними умовами, що підвищить ефективність розвідки та зменшить витрати.

Ключові слова: *нафтогазові родовища, маспектрометрія індуктивно-зв’язаної плазми, геохімічний метод, міграція вуглеводнів, розвідувальна свердловина*

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