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Research Paper

Hydrogeochemical Modeling of Mineral Processes in Hot Springs and Mine Waters

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Abstract

Understanding hydrogeochemical processes is essential for predicting mineral alteration and carbonate scaling in geothermal and mining environments. However, such studies remain limited in Malifut, North Maluku, where geothermal manifestations and mining activities coexist. This study aims to classify hydrochemical facies and evaluate mineral stability in various thermal waters, including underground mine waters, a hot spring, and borehole thermal waters. Field measurements of temperature, pH, electrical conductivity, and total dissolved solids were conducted, while major ions were analyzed using ion chromatography. Hydrochemical facies were identified using the Cl–SO_4–HCO_3 ternary diagram, and mineral saturation indices were modeled with PHREEQC. The classification revealed that borehole waters belong to the peripheral type, while Shallut and Kencana mine waters are steam-heated, and Toguraci, together with Akesahu hot spring, are volcanic waters. PHREEQC modeling revealed that volcanic and steam-heated waters are oversaturated with calcite and aragonite, indicating a strong potential for carbonate precipitation due to CO_2 degassing and elevated temperatures. Borehole waters were mostly near equilibrium or undersaturated, except PZ-8, which exhibited dolomite oversaturation and a clear geothermal signature. All samples were undersaturated with gypsum and anhydrite, indicating carbonate equilibria as the dominant control. This integrated approach enhances the understanding of water–rock interaction, fluid origin, and scaling risk in geothermal–mining systems, and provides practical insights for water management and scaling mitigation strategies in Malifut.

Keywords *Hydrogeochemistry, Geothermal, Phreeqc, Water–Rock Interaction*

INTRODUCTION

Hydrogeochemical processes govern the interaction between geothermal fluids, host rocks, and mining environments. The chemical composition of thermal waters, often enriched in dissolved gases and major ions, controls mineral alteration and precipitation, influencing underground mining operations and borehole stability. In geothermal systems, water chemistry is primarily affected by magmatic inputs, steam heating, and meteoric water mixing, which can be evaluated through hydrochemical facies analysis (Nicholson, 2012).

Geochemical modeling, particularly using PHREEQC, is widely applied to quantify aqueous speciation, mineral saturation states, and gas–water equilibria under various physicochemical conditions (Appelo & Postma, 2004; Parkhurst & Appelo, 2013). Such modeling enables assessment of carbonate precipitation, scaling potential, and water–rock interactions in geothermal fields (Sanliyuksel & Baba, 2011). Recent studies emphasize the importance of coupling hydrochemical

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facies analysis with numerical modeling to interpret the dynamics of carbonate precipitation and CO_2 degassing behavior in geothermal fields (Benavente et al., 2025).

In Malifut, North Maluku, geothermal manifestations and underground mining occur within the same system, yet the hydrogeochemical characteristics and mineral stability of its waters remain insufficiently studied. Despite several reports describing general water chemistry and facies distribution (Firmansyah et al., 2025), detailed hydrogeochemical modeling of mineral precipitation potential and carbonate equilibria remains limited. This knowledge gap constrains the understanding of mineral scaling processes that could affect both geothermal exploration and mine-water management.

Therefore, this study integrates hydrochemical facies classification with PHREEQC-based modeling to determine alteration and precipitation minerals in underground mine waters, a hot spring, and borehole thermal waters in Malifut. The results aim to clarify the geochemical behavior of these waters, assess scaling potential, and provide a scientific basis for water management and mitigation strategies in geothermal mining environments.

LITERATURE REVIEW

PHREEQC for Hydrogeochemical Modeling and Saturation Indices

PHREEQC is a widely used geochemical code for speciation, mineral saturation, and reaction-path modeling in groundwater, geothermal, and mine-water systems. It enables calculation of aqueous speciation, mineral solubility, and gas–water equilibria under various physicochemical conditions, supporting the assessment of carbonate equilibria and scaling risk (Parkhurst & Appelo, 2013). The software's ion-association approach performs well under typical ionic strengths of groundwater and mine waters; however, caution is needed as salinity levels increase.

Carbonate Equilibria and Indicators of Precipitation Potential

In hydrothermal and mine-water settings, positive SI values for calcite and aragonite commonly indicate oversaturation and a thermodynamic drive toward carbonate scaling/precipitation. Numerous PHREEQC-based studies report oversaturation of $CaCO_3$ polymorphs across seasons and flow paths, using SI as a proxy for precipitation tendency and for interpreting water–rock interaction and degassing effects (Reyes-Santiago et al., 2021). Methodological standards and recent syntheses reinforce using SI alongside complementary metrics (e.g., pCO_2) to evaluate scaling risk and carbonate system behavior, which is directly pertinent when contrasting hot springs, underground mine waters, and borehole thermal waters (Benavente et al., 2025; Tang et al., 2021).

Hydrogeochemistry of Mine Waters

Mine-water geochemistry is shaped by mixing, carbonate/sulfate equilibria, and rebound processes after dewatering. Classic and recent reviews emphasize carbonate precipitation as a frequent process that governs alkalinity and metal mobility, with modeling frameworks (often using PHREEQC) to simulate mixing and mineral reactions. These insights are essential for interpreting SI patterns in underground water samples from active mines (Huisamen & Wolkersdorfer, 2016).

Hydrogeochemistry of Hot Springs and Geothermal Systems

Comparative studies of hot springs commonly use PHREEQC to couple major-ion chemistry with SI (calcite/aragonite/dolomite, gypsum/anhydrite) and with geothermometry/isotope tools to infer subsurface processes and reservoir conditions. This body of work provides transferable interpretation logic when positioning hot springs versus mine and borehole waters along a thermal–chemical gradient (Ma et al., 2024).

RESEARCH METHOD

The study was conducted in the Malifut district, North Maluku, Indonesia, a region characterized by mineralized volcanic rocks, geothermal manifestations, and active underground mining operations. Thermal waters in this area are found in various environments, including natural hot springs, underground mine waters, and exploration boreholes that intersect geothermal gradients.

Sample Collection

A total of twelve water samples were collected from different hydrogeological settings in the Malifut District, North Maluku (Figure 1). These included three underground mine waters (Shallut, Toguraci, and Kencana), one hot spring (Akesahu), and eight samples from four geothermal boreholes at top and bottom intervals. Sampling campaigns were conducted from February to May 2023, covering the transition from the wet to dry season to capture representative hydrogeochemical conditions.

Sampling procedures followed the Indonesian National Standard (SNI, 2021) – Method of Water Sample Collection for Physical and Chemical Testing, ensuring reliable and reproducible sample quality. Field parameters, including temperature, pH, electrical conductivity (EC), and total dissolved solids (TDS), were measured in situ using calibrated portable meters prior to sampling. All water samples were immediately filtered through 0.45 μm membrane filters and stored at 4 °C until laboratory analysis to prevent chemical alteration during transport and storage.

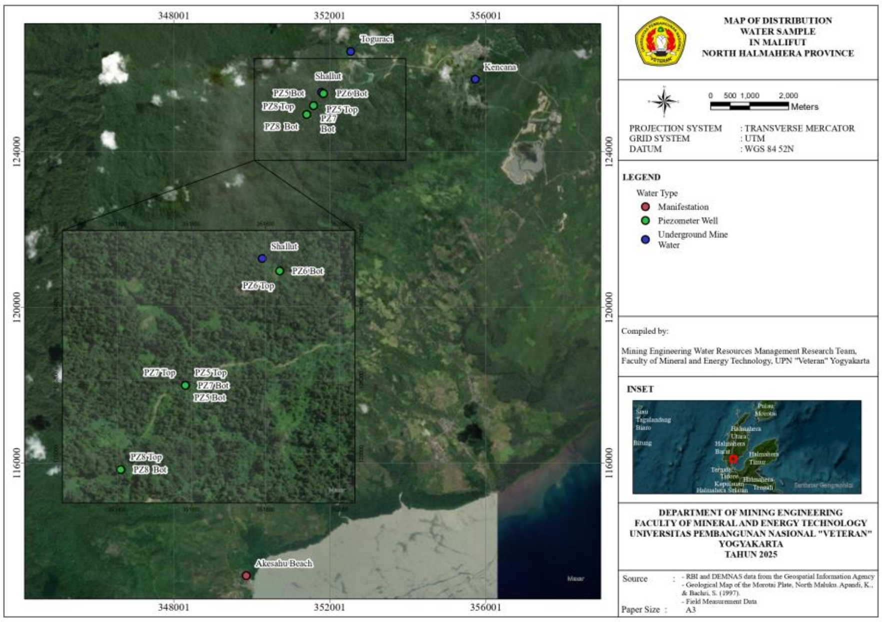

Figure 1. Water Sampling Map

Laboratory Analysis

Major cations and anions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, Cl^{-}) were determined using ion chromatography (IC), while the anion HCO_3^- was measured by titration. Charge balance error (CBE) was calculated to assess analytical accuracy, and only samples with CBE within ±5% were used in the modeling (Appelo & Postma, 2004).

Geochemical Modeling with PHREEQC

Geochemical modeling was conducted using PHREEQC version 3 (Parkhurst & Appelo, 2013) with the phreeqc.dat and wateq4f.dat thermodynamic databases. Field and laboratory data (temperature, pH, EC, and major ion concentrations) were used as input to calculate aqueous speciation and mineral saturation indices (SI). The SI values indicate mineral stability conditions: SI > 0 suggests oversaturation (tendency to precipitate), SI < 0 indicates undersaturation (tendency to dissolve), and SI ≈ 0 represents near-equilibrium conditions (Bethke, 2022). A comparative analysis was conducted to evaluate the differences among underground mine waters, hot spring waters, and borehole thermal waters. Particular attention was given to carbonate minerals (calcite and aragonite), which often control scaling and alteration processes in geothermal and mining environments.

FINDINGS AND DISCUSSION

Field measurements show distinct spatial variations in temperature, total dissolved solids (TDS), and pH across the studied waters (Figure 2–4). Table 1 provides information on the temperature range, which varies from 32.9 °C (PZ5 Top) to 69.7 °C (Toguraci), with the hottest waters observed in the Toguraci underground mine water and Akesahu hot spring, indicating a strong geothermal input. Borehole waters display depth-dependent temperature variations, with higher values in deeper intervals such as PZ8 Bot (61.6 °C).

TDS shows a similar trend, with the highest concentrations at Akesahu (2130 ppm) and Toguraci (1630 ppm), moderate values at Kencana, and lower concentrations in Shallut and most boreholes, reflecting meteoric dilution. pH values range from 7.06 to 8.16, mostly neutral to slightly alkaline, with lower pH in geothermal centers (e.g., Toguraci, 7.10) and higher values in peripheral waters (e.g., PZ8 Bot, 8.16). These patterns highlight the combined effects of geothermal input, gas dissolution, and mixing processes.

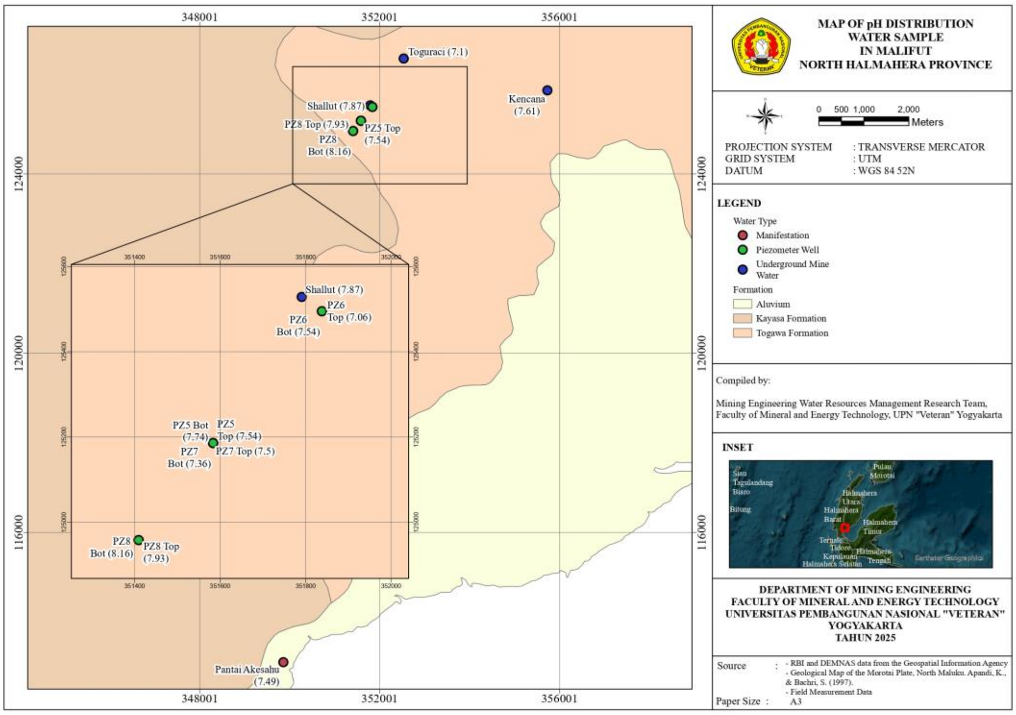

Figure 2. Map of pH Distribution

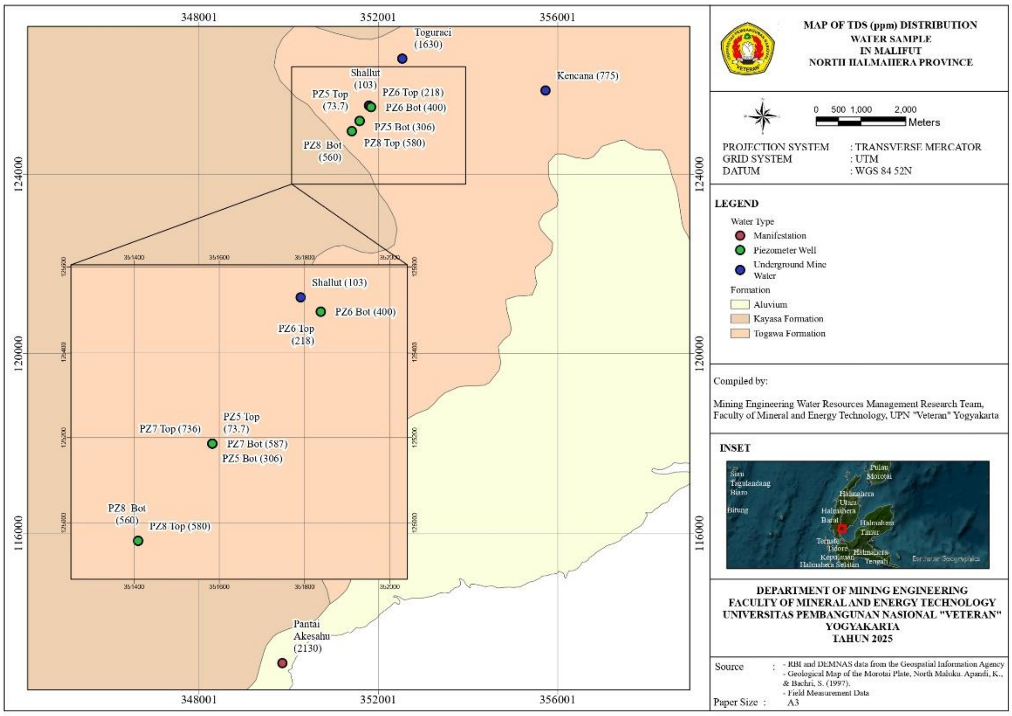

Figure 3. Map of Total Dissolved Solid (TDS) Distribution

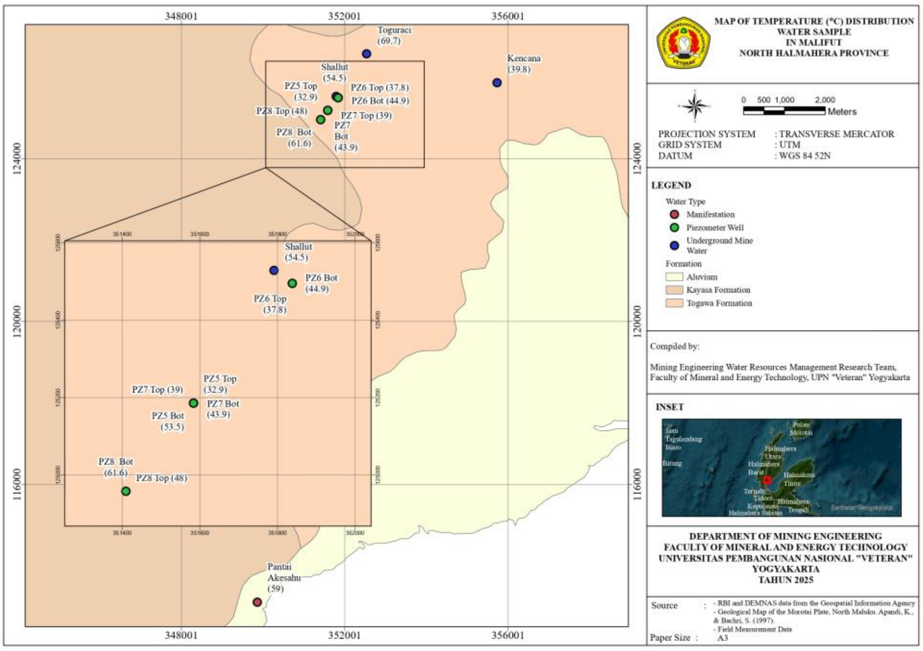

Figure 4. Map of Temperature Distribution

The $Cl–SO_4–HCO_3$ ternary diagram (Figure 5) clearly differentiates the studied waters. Borehole thermal waters plot within the peripheral field, suggesting strong mixing with meteoric or shallow groundwater despite their elevated temperatures. In contrast, underground mine waters from Shallut and Kencana fall within the steam-heated field, indicating the influence of steam condensation and subsequent oxidation of H_2S. In contrast, Toguraci underground water and the Akesahu hot spring fall within the volcanic water field, consistent with input from deeper hydrothermal fluids rich in Cl^- and SO_4^{2-}.

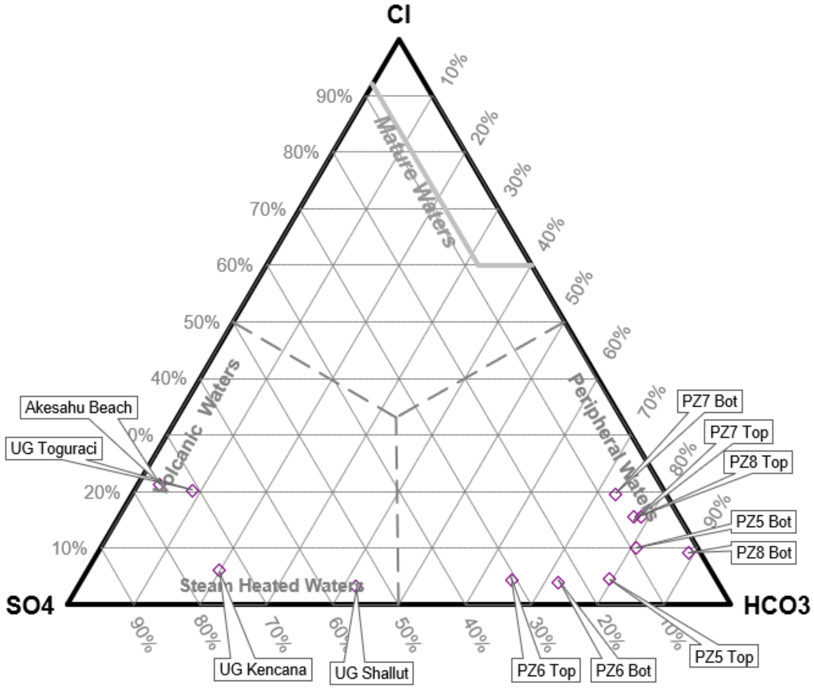

Figure 5. Ternary Diagram $Cl–SO_4–HCO_3$ of the Water Sample

The ternary classification provides important insights into hydrothermal processes that complement the PHREEQC modeling. Peripheral waters, such as the borehole samples, typically represent groundwater that has been heated but has not undergone significant magmatic gas input, which explains why these samples exhibit lower saturation indices for carbonate minerals compared to volcanic waters. This agrees with interpretations that peripheral waters reflect mixing with shallow groundwater or lateral outflows of geothermal systems (Nicholson, 2012).

Steam-heated waters, such as those from Shallut and Kencana underground mines, are commonly associated with the condensation of magmatic steam near the surface, followed by oxidation of H_2S to SO_4^{2-}. This process produces waters enriched in sulphate, with moderate chloride and bicarbonate contents. The occurrence of steam-heated waters in underground mine workings suggests active interaction between geothermal gases and shallow aquifers, consistent with observations in similar volcanic terrains (Firmansyah et al., 2025; Sanliyuksel & Baba, 2011). Volcanic waters, such as those observed at Toguraci and Akesahu, are characterized by high chloride and sulphate concentrations, reflecting direct contributions from deep-seated hydrothermal fluids and magmatic volatiles (e.g., CO_2, H_2S). These waters typically show higher pCO_2 and enhanced mineral dissolution, resulting in carbonate oversaturation in the PHREEQC modeling. Their classification as volcanic waters supports the interpretation that the Akesahu hot spring is one of the closest discharges to the geothermal source. Similar volcanic-type waters have been documented in geothermal systems worldwide, including those in Indonesia (Nicholson, 2012).

Twelve thermal-water samples, which are shown in Table 1 from Malifut (3 underground mine waters—Shallut, Toguraci, Kencana; 1 hot spring—Akesahu; 8 borehole waters from four piezometers, top/bottom) were speciated with PHREEQC v3 to compute mineral saturation indices (SI). SI>0 implies oversaturation (thermodynamic drive to precipitate), SI≈0 near-equilibrium, and SI<0 undersaturation. This interpretation follows PHREEQC documentation and standard geochemical practice (Parkhurst & Appelo, 2013).

Table 1. Chemical Characteristics and Saturation Index of Water Sample

				Saturation Index (PHREEQC)				
No	**Sample Name**	**Temp (°C)**	**pH**	**Carbonate**			**Sulphate**	
				Aragonite	**Calcite**	**Dolomite**	**Anhydrite**	**Gypsum**
1	UG Shallut	54.5	7.87	0.09	0.3069	-0.8627	-1.8593	-1.8601
2	UG Toguraci	69.7	7.1	0.0281	0.3108	-0.9976	-0.5213	-0.667
3	UG Kencana	39.8	7.61	0.0536	0.2231	-0.8893	-1.2472	-1.1005
4	Akesahu Beach	59	7.49	0.1139	0.3487	-1.8677	-0.3981	-0.443
5	PZ6 Top	37.8	7.06	-1.6032	-1.4386	-3.1896	-3.1167	-2.949
6	PZ6 Bot	44.9	7.54	-0.7382	-0.5544	-1.4795	-2.9111	-2.8164
7	PZ8 Top	48	7.93	0.766	0.9596	1.1711	-2.5404	-2.4771
8	PZ8 Bot	61.6	8.16	0.9498	1.1956	1.5923	-3.1136	-3.183
9	PZ5 Top	32.9	7.54	-1.1208	-0.9664	-2.147	-3.4765	-3.2572
10	PZ5 Bot	53.5	7.74	-0.2337	-0.0207	-0.4007	-3.0858	-3.0768
11	PZ7 Top	39	7.5	-0.0464	0.1211	Not identified	-2.816	-2.661
12	PZ7 Bot	43.9	7.36	0.0067	0.1875	Not identified	-2.5707	-2.4661

Carbonate Saturation and Precipitation Potential

Underground waters (Shallut, Toguraci, Kencana) and the Akesahu hot spring show oversaturation with respect to calcite and aragonite (SI > 0), indicating strong potential for carbonate precipitation. This is consistent with CO_2 degassing and elevated temperatures driving pH increase and shifting carbonate equilibria (Hamdi & Tlili, 2024; Zacherl & Baumann, 2023). Similar oversaturation patterns have been reported in other geothermal fields, such as Baoshan, China (Ma et al., 2024).

Borehole waters show variable SI patterns. PZ-6 waters are undersaturated, indicating minimal scaling risk, while PZ-5 and PZ-7 range from near-equilibrium to slightly oversaturated. PZ-8 is the most thermally influenced borehole, showing oversaturation not only for calcite and aragonite but also for dolomite (SI > 1). This suggests proximity to a geothermal source and enhanced degassing, aligning with observations from other geothermal boreholes (Hu et al., 2022).

Kinetic Limitations on Dolomite Formation

Although thermodynamic modeling indicates dolomite oversaturation in PZ-8, kinetic barriers such as Mg^{2+} hydration and structural ordering often prevent precipitation at moderate temperatures. Dolomite formation typically requires extended residence times, catalytic surfaces, or specific water chemistries (Chen et al., 2023). This means that calcite and aragonite scaling are more likely to dominate in the current hydrogeochemical setting.

Sulphate Mineral Stability

All samples are undersaturated with respect to gypsum and anhydrite (SI < 0), indicating negligible potential for sulphate scaling under present conditions. Similar undersaturation behavior is commonly observed in geothermal systems, where Ca^{2+} and SO_4^{2-} activities remain below solubility limits (Benavente et al., 2025). Overall, the integration of hydrochemical facies analysis and PHREEQC modeling provides a comprehensive understanding of water–rock interactions and scaling potential across the studied hydrothermal environments. The results reveal distinct geochemical behavior between peripheral, steam-heated, and volcanic waters in Malifut. Importantly, the identification of dolomite oversaturation in PZ-8 is a novel finding that indicates a stronger geothermal influence than previously recognized. These insights can support the design of monitoring and scaling mitigation strategies in geothermal and mining operations, a perspective that has not been addressed in earlier studies of the region (Firmansyah et al., 2025).

CONCLUSIONS

This study combined hydrochemical facies classification and PHREEQC-based modeling to investigate mineral alteration and precipitation processes in geothermal and mining waters from Malifut, North Maluku. The results show that borehole waters are classified as peripheral types, while Shallut and Kencana mine waters are classified as steam-heated types, and Toguraci, together with Akesahu hot spring, is classified as a volcanic type. Volcanic and steam-heated waters are oversaturated with respect to calcite and aragonite, indicating a strong tendency for carbonate precipitation driven by CO_2 degassing and elevated temperatures. Most borehole waters are near equilibrium or slightly undersaturated, except PZ-8, which shows dolomite oversaturation and a distinct geothermal signature. All water samples are undersaturated with gypsum and anhydrite, confirming that carbonate equilibria dominate the mineral stability in the system. The novelty of this research lies in identifying dolomite oversaturation in the peripheral borehole waters of Malifut, which indicates a more extensive geothermal influence than previously recognized. This finding enhances the understanding of hydrogeochemical processes and mineral stability in interconnected geothermal–mining environments.

LIMITATIONS & FURTHER RESEARCH

This study is limited to equilibrium modeling based on major ion data. Kinetic aspects, trace metal concentrations, and isotopic compositions were not evaluated and may influence the interpretation of mineral equilibria. Future research should incorporate isotopic tracers, reactive-transport modeling, and temporal monitoring to characterize better the dynamic interactions and scaling behavior of geothermal and mining waters in Malifut.

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