

Dear Editorial Office of HESS and Prof. Dai

We wish to express our sincere gratitude for the editorial team's diligent handling of our manuscript and extend particular appreciation to Prof. Dai for your judicious oversight throughout the review process. Your constructive decision letter has provided us the opportunity to enhance the manuscript's scientific rigor. In response to the insightful comments from two reviewers and two domain experts, we have thoroughly revised the manuscript. All the revised contents have been marked in **red** in the manuscript.

Major revisions include:

1. Clarified the study's conclusion: Pre-seismic groundwater anomalies (whitening, turbidity) are caused by dissolution of anhydrite and carbonate minerals.
2. Strictly controlled overinterpretation: Dissolution of target horizons reflects water-rock interaction intensity, potentially driven by seasonal rainfall changes or fault zone activity.
3. Defined the contribution: Establishing early warning systems for geohazards by identifying region-specific target indicator horizons (e.g., anhydrite), implementing their continuous monitoring, and developing localized evaluation metrics.
4. Assessed potential anthropogenic impacts in the study area.
5. Added the Cl^- - SO_4^{2-} - HCO_3^- ternary diagram (Fig. S3).
6. Specified that blue symbols in Fig. 3 represent snowmelt-derived waters, with supporting citations.
7. Proposed solutions for unresolved issues:
 - (1) Quantifying anhydrite concentration thresholds for seismic warnings;
 - (2) Disentangling interference from rainfall/human activities via continuous monitoring;

We have proposed actionable solutions and delineated potential future research directions.

In short, after fully and effectively communicating with the reviewers, we modified the possible problems in our manuscript according to the suggestions of the

reviewers, so that the analysis of data in the manuscript is more rigorous and the extension is appropriate

We sincerely wish the current version meets your standards and welcome further guidance.

Finally, I would like to thank HESS editorial Department and Dai Editor-in-Chief for their hard work

Sincerely

Zebin Luo

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Point-by-point response to comments:

Note: *Italic blue* is the comment. Black is the reply, and **important sentences are bolded**.

Red indicates the position of the modification information in the newly submitted revised draft.

Reply to referee comments

Anonymous Referee #3

*nominated 08 May 2025, accepted 12 May 2025, report 28 May 2025***Report #1**

Manuscript Title: Anhydrite Dissolution Dynamics as a Hydrogeochemical Tracer of Seismic-Fluid Coupling: Insights from the East Anatolian Fault Zone, Turkey

General Comment:

This study investigates hydrogeochemical anomalies along the East Anatolian Fault Zone (EAFZ), integrating a 13-year groundwater dataset (2013–2023) with post-seismic responses to the 2023 Mw 7.8 and 7.6 earthquakes. The authors propose anhydrite dissolution dynamics as a potential tracer for fault activity, supported by spatial variations in groundwater chemistry and PHREEQC modeling. The topic is scientifically significant, and the dataset is comprehensive, offering valuable insights into fault-controlled fluid-rock interactions. However, the manuscript lacks a robust

theoretical framework to quantitatively link hydrogeochemical anomalies to tectonic processes, limiting its broader applicability. Below are specific concerns and recommendations for improvement.

Reply: Thanks! We thank you for these constructive critiques. Revisions strictly adhere to:

1. Empirical boundaries (no overclaimed causality)
2. Regional focus (no unjustified global extrapolation)
3. Actionable next steps (lines 416-417)

Your insights have significantly strengthened the manuscript's scholarly integrity.

1. While the manuscript meticulously documents spatial hydrogeochemical variations (e.g., Na-Cl vs. Ca-HCO₃ waters) and associates SO₄²⁻ anomalies with anhydrite dissolution, the causal relationship between seismic stress and dissolution dynamics remains largely descriptive. Critical gaps include (1) Stress-Permeability-Reaction Coupling. The assertion that "seismic stress redistribution induces fracture network reorganization" lacks quantitative validation. A mechanistic model linking stress changes to permeability evolution, fluid flow, and anhydrite dissolution rates is absent. (2) Climate-Tectonic Signal Separation: Although climatic influences (e.g., rainfall) are acknowledged, no methodology is provided to disentangle tectonic signals from climatic noise. Statistical or machine learning approaches (e.g., PCA, random forests) could enhance signal discrimination.

Reply: Thanks! We fully acknowledge this limitation. While our study identifies anhydrite as a potential seismic tracer through spatial correlations, quantitative validation of stress-permeability-reaction coupling requires further research. As noted in the Discussion (Section 5.4), we have: 1) Explicitly stated this gap as a key future research priority. 2) Proposed targeted experiments (e.g., high-P/T reaction kinetics) to address it. Your suggestion for machine learning approaches is valuable and will guide our ongoing work. (lines 410-418)

2. The PHREEQC simulations, while useful, are inadequately described. Key parameters (e.g., boundary conditions, reaction pathways, temperature-pressure regimes) and sensitivity analyses are omitted, hindering reproducibility. Furthermore,

the simulations focus on equilibrium states, neglecting transient effects of seismic perturbations (e.g., rapid fluid pressure changes).

Reply: Thanks! We agree that PHREEQC has inherent limitations in modeling seismic transience. However:

1. Batch-reaction simulations (modified from magmatic partial melting models) effectively approximate sudden chemical shifts by adjusting reactant inputs.
2. **Transient effects fall beyond this study's scope given our non-continuous dataset (2013–2023).**

The core of our research lies in revealing the groundwater circulation and water-rock interaction process of the entire EAFZ. Through this, we have discovered that the dissolution of anhydrite may be affected by seismic activities. The transient effects will be further studied and quantified in subsequent high-temperature and high-pressure experiments simulating water-rock interaction or in the continuous monitoring studies of natural samples.

3. The manuscript proposes anhydrite dissolution as a tectonic tracer but fails to establish quantitative thresholds or metrics for anomaly detection. Critical questions remain unanswered: What magnitude of SO_4^{2-} concentration change constitutes a tectonic signal? How do response times of anhydrite dissolution align with seismic cycles (e.g., foreshock, coseismic, postseismic phases)?

Reply: Thanks! We maintain that regional heterogeneity prevents universal thresholds:

- 1) PHREEQC confirms anhydrite dissolution contributes 30–100% to SO_4^{2-} anomalies (Section 5.2.1).
- 2) However, tectonic signals cannot be isolated by concentration thresholds alone due to multi-source mixing (e.g., seawater, carbonates) and Climate interference.
- 3) **Our core contribution lies in proposing anhydrite as a regional "target indicator" – its abrupt changes may signal permeability shifts.**
- 4) Continuous long-term monitoring requires a significant investment of manpower and resources. Currently, this work has been piloted in the western Sichuan region.

4. The study's novelty - prioritizing shallow water-rock interactions over deep fluid signals - is underemphasized. Comparisons with global analogs (e.g., San Andreas

Fault, Himalayan frontal thrusts) are lacking, limiting the broader relevance of anhydrite as a tectonic tracer. Additionally, the advantages and limitations of anhydrite versus traditional tracers (e.g., He isotopes, Rn anomalies) are not critically discussed.

Reply: Thanks! We clarify two key points:

1. Regional specificity: **Anhydrite's applicability is context-dependent** (e.g., evaporite-rich EAFZ).
2. Paradigm shift: The innovation is methodological – identifying region-specific target horizons (e.g., anhydrite here, serpentine elsewhere) for localized monitoring. We proposed that traditional tracers (He, Rn) and anhydrite serve complementary roles; multi-proxy approaches are essential for earthquake forecasting.

Anonymous Referee #4

nominated 08 May 2025, accepted 15 May 2025, report 11 Jun 2025 Report #2

The authors analyzed the post-earthquake groundwater samples and compared them with the pre-earthquake dataset over the past 13 years, and attempted to discuss the post-earthquake hydrochemical changes and their mechanisms.

Unfortunately, I do not agree with the claims presented in this manuscript. However, I could understand the scientific significance of the samples collected, and I agree with the other reviewer's comments "The data could be used to create a simply report without stressing the potential of gypsum as earthquake tracer. The data could be used for future researches in the area. I don't know if there is a form in which this could be done for this journal. Maybe the editor can suggest solutions."
<https://doi.org/10.5194/hess-2024-395-RC2>

Reply: Thanks! We are grateful for your recognition of our data. The revised manuscript fundamentally differs from the original submission. With clearer arguments, robust evidence, and logical rigor, we wish its publication in HESS will advance research on groundwater anomalies and earthquake mechanisms, offering new perspectives for seismic forecasting.

Manuscript Logic Overview:

1. Question Raised:

Pre-seismic anomalies (whitening, turbidity, intermittent surges) observed ~1 month before the 2023 Turkey double earthquakes. What caused these? Could they relate to seismicity?

2. Hypothesis:

Chemical anomalies (whitening/turbidity) stem from hydrochemical changes; Intermittent gushing reflect stress variations. These may result from seismic disruption of hydrogeological equilibrium.

3. Data & Findings:

Integrated 13-year pre-seismic data with post-seismic (1-month) measurements.

Anomalous wells or groundwater (HS04/HS14) showed elevated (Table 1) (lines 170-171):

EC: 1305–2683 $\mu\text{S}/\text{cm}$

Ca^{2+} : 151.43–501.58 mg/L

SO_4^{2-} : 229.75–316.61 mg/L

PHREEQC modeling revealed EAFZ segmentation:

North: Shallow/deep mixing (igneous water-rock interactions)

Central-South: Shallow circulation (anhydrite/carbonate dissolution; seawater influence)

Earthquake occurred in central-south: anhydrite/carbonate dissolution likely caused anomalies.

4. Key Evidence:

Reservoir temperatures (156–234°C) estimated by SiO_2 -Eh model and saturation index calculated by PHREEQC confirm anhydrite is supersaturated when the temperature exceeds 150°C at HS04 and HS14 samples this study. (Fig. 7 in manuscript) (lines 298-303).

$^{87}\text{Sr}/^{86}\text{Sr}$ mixing models: Evaporite (anhydrite/gypsum) input in central-south groundwater (Fig. 5 in manuscript) (lines 260-266).

Geothermal gases: Higher crustal contribution to geothermal gases in central-south vs. north.

Geologic background: Carbonate/evaporite deposits near HS14 (e.g., amik lake—a paleo-saline lake deposit 20 km away).

5. Conclusion:

Pre-seismic anomalies resulted from seismically disrupted hydrogeological equilibrium. Anhydrite/carbonates are primary contributors, serving as potential tracers of water-rock interaction anomalies. Further investigation into their relationship with seismogenesis is warranted.

The reasons for this comment are as follows:

The first issue is the lack of insight into hydrological processes. Generally, spring discharge mechanisms are related to regional groundwater flow systems based on geological and topographical settings, seasonal precipitation patterns, and

anthropogenic activities (e.g., groundwater extraction, urbanization, and land use change). However, the discussion proceeds without clarifying the sampling locations or the hydrogeological information of the regions. A description of the regional groundwater flow system, including the discharge process for the collected springs, is essential for discussing the abnormality of the collected samples. This issue also sensed the choice of the surface geological map, which contained indistinct geological information regarding the area surrounding the sampling sites.

Reply: Thanks! The issue you raised is something that must be taken into consideration. That's why we were very cautious when choosing the geological maps.

We confirm the geological map's validity:

Source: Geological map of EAFZ, modified from van Hinsbergen et al. (2024, EPSL)(<https://doi.org/10.1016/j.epsl.2024.118827>). Original source of the map: Turkish government (MTA, *1:500,000 Geological Map*; <https://www.mta.gov.tr/en/maps/geological-500000>). (lines 72-76)

Anthropogenic Influence Ruled Out:

Sampling sites are remote (far from cities/factories; Video 1).

Trace elements (e.g., Pb) show consistent patterns (Fig. S3), excluding regional contamination (lines 160-163).

Even if detailed descriptions of groundwater storage and flow conditions in the entire EAFZ during normal (non-seismic) conditions are added, it cannot be specified whether the obtained hydrochemical features were determined for seismic events. This is because localized points exhibiting geochemical anomalies of geothermal origin might exist even under non-seismic conditions owing to subsurface geological heterogeneity. Therefore, it is important to present direct evidence through continuous sampling and analysis at the same location to determine whether water chemistry anomalies are caused by earthquakes.

Reply: Thanks! We fully align with your perspective. To prevent overinterpretation, we have rigorously constrained the manuscript's conclusions to emphasize that:

Anhydrite dissolution solely demonstrates its capacity as a tracer for variations in water-rock interaction intensity.

Regarding causality:

No definitive link to seismicity has been established.

The post-seismic sampling timing (1 month after the event) led us to cautiously propose a hypothesis that tectonic activity may drive such intensity changes.

Consequently:

All seismic linkages are explicitly framed as testable propositions.

We outline specific future research priorities to validate this mechanism (Section 5.4) (lines 365-422).

Another issue is the academic contribution to the current scientific challenges in earthquake prediction. Earthquake precursors in natural systems are relatively universal; however, their forms are diverse and predictive information that can be used for short-term earthquake prediction has not yet been clearly identified. This represents the general state of academic research on earthquake prediction (<https://doi.org/10.1126/science.adi8032>).

Reply: Thank you for the literature materials you provided. We have added relevant citations (lines 357-358). We are well aware that earthquake prediction is one of the major challenges faced by humanity, and this is also the driving force behind our progress

I strongly agree that changes in the water chemistry components of groundwater have been widely reported and discussed as precursors to large earthquakes. However, there is a lack of specific mention of the scientific difficulties necessary to elevate this precursor phenomenon in earthquake-prediction technology. While the reasons “climate factors” in the introduction and “funding shortages” in the discussion section are cited as related issues, it seems necessary to point out specific scientific challenges, such as the scale and frequency of effective water chemistry observation networks. Furthermore, the manuscript should explain how the discussions within the paper contribute to addressing these challenges.

Reply: Thanks! Thank you for your recognition of the view that groundwater has the potential to be one of the means for earthquake prediction. Thank you for your suggestion. We have added relevant expressions: “We have proposed that an

abnormality in groundwater chemical components, which does not require the involvement of deep fluids, could potentially serve as a basis for earthquake prediction” (lines 67-69).

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Based on the above reasons, I conclude that it is difficult to resolve the issues mentioned above using the data collected by the authors and the data presented in the literature. However, the presented dataset is useful for discussing the possible hydrochemical evolution processes. The discussion in the manuscript is also useful for proposing conceivable mechanisms. I would like to provide specific comments on the improvement. I hope that the authors will use them to advance the manuscript, regardless of the decision.

Reply: Thanks! We sincerely appreciate your recognition of our work. As noted, certain original phrasings may have inadvertently misrepresented our intent. Following your expert and constructive suggestions, we have meticulously refined the manuscript to eliminate ambiguities arising from linguistic imprecision.

The revised version now presents:

Unequivocal arguments with a logically coherent evidence chain

Compelling implications for advancing groundwater-seismicity research

While continuous pre-seismic monitoring remains logistically unfeasible (given the unpredictable nature of earthquakes), we acknowledge its scientific necessity. Pilot programs like the ongoing large-scale automated sampling in Western China’s seismic zones (Sichuan Province) exemplify potential solutions, though such initiatives face significant technical and budgetary constraints.

Specific Comments

1. There are two types of earthquake predictions: “Probabilistic forecasting” and “Deterministic prediction” (<https://doi.org/10.4401/ag-5350>). It would be better to explain the type of prediction that is the focus of this study.

Reply: Thanks! Thanks for the provided literature materials. Our current research is a probabilistic prediction. We have added relevant citations (lines 367-370).

2. HS04 is described as a monitoring well in L55; however, in Table 1, it is shown as S,

which indicates spring water.

Reply: Thanks! We provided detailed instructions for the sampling points. (lines 16, 58, 170-171, 274)

3. The water temperature of the data presented as hot springs in Table 1 was not particularly high. What definition was used to classify them as 'hot springs'?

Reply: Thanks! Thank you. We checked the types of the water samples in Table 1. (lines 171-170)

4. Generally, spring discharge temperature reflects the average air temperature in the recharge area (Table 1). The differences in temperature between the samples seemed to reflect specific hydrological processes.

Reply: Thanks! Thank you for your suggestion. We have added the relevant expressions. (lines 137-138)

5. Are there any available spring discharge rate information?

Reply: Thanks! Regrettably, we were unable to measure the relevant parameters.

6. Table 1 does not include δD values; however, Fig. 3 is included, which is inconsistent.

Reply: Thanks! Thank you very much for pointing out our mistakes. We have added the δD data to Table 1. (lines 170-171)

7. L182: To avoid the misunderstanding, what observation is "Pre-seismic groundwater anomalies" to be specified is better.

Reply: Thanks! We have added detailed explanations. "(white water, turbidity and intermittent groundwater gushing) (Video S1 and Video S2)" (lines 192-193)

8. The water temperature and electrical conductivity may be influenced by mixing with groundwater from different sources. How much variation do these data vary under normal conditions?

Reply: Thanks! The variation range of EC is 275 - 2683 $\mu\text{S}/\text{cm}$. (lines 133-134)

9. An insufficient explanation is for the red-shaded areas extending from the magma fluid distribution shown in Fig. 3. What do the blue plots indicate at the endpoints?

Reply: Thanks! The red magma area is an area of intermediate-acidic magmatic rocks (Karaoğlu et al., 2020 Lithos, <https://doi.org/10.1016/j.lithos.2020.105524>). Considering the magma activity characteristics of the eastern plateau of Turkey, the

range adopted (Giggenbach, 1992) is reasonable ($\delta D = -30$ – -10 ; $\delta^{18}O = 8$ – 12). Snow water ($\delta D = -115$ ‰, $\delta^{18}O = -16.3$ ‰) from (Andy et al., 2020) (The sampling elevation is approximately 2000m). (lines 164-169)

10. What specific samples did clear $\delta O18$ enrichment at L191 refer to? Did all the northern groundwater show enrichment?

Reply: Thanks! We have optimized the description here. “In contrast, **some** northern groundwater displays distinct $\delta^{18}O$ enrichment deviating from local meteoric trends” (lines 202)

11. To discuss the spatial heterogeneity of major dissolved ions at L198, it is necessary to confirm not only the spatial distribution of the trilinear diagrams showing composition ratios but also the spatial distribution of the hexagonal diagrams showing concentrations.

Reply: Thanks! We have included relevant diagrams in the Supporting Information (Fig. S1) (lines 144).

12. The 13-year dataset presented in Fig. 2 and 3 shows considerable variations in the major ion compositions and stable isotope ratios. I believe that The three regional divisions shown in the legend are insufficient to explain the reasons for this variation.

Reply: Thanks! Indeed, spatial variations in chemical composition are governed by regional lithology, which controls the sources of major ions in groundwater. Conversely, stable isotope signatures ($\delta^{18}O$ and δD) reflect recharge processes and mixing of multiple source waters, governing the origin of groundwater itself.

Thus:

Fig. 2 demonstrates hydrochemical differences driven by lithological heterogeneity.

Fig. 3 reveals isotopic patterns dominated by continental effects – notably progressive depletion in heavier isotopes with increasing distance from the Mediterranean Sea.

These complementary datasets provide mutually consistent explanations of groundwater evolution processes across the EAFZ.