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# Hydrothermal mobilization of heavy rare earth elements in carbonate-rich systems: Implications from the Arıklı mineralization (NW Türkiye)

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ABSTRACT

The mobilization and enrichment of heavy rare earth elements (HREE) in carbonate-hosted hydrothermal systems remain poorly constrained due to limited thermodynamic and experimental data. This study re-evaluates the Arıklı Th–U–HREE mineralization in northwestern Türkiye to explore the geochemical plausibility of late-stage fluid–rock interaction and ligand-controlled speciation processes in carbonate-bearing environments. Modeling of solubility trends suggests that moderate-temperature (120–180 °C), moderately alkaline (pH 10–11) fluids may facilitate the transport of HREE via carbonate–hydroxyl complexation. These inferred conditions are consistent with recent experimental and thermodynamic studies, indicating that late-stage HREE redistribution could occur without the direct involvement of high-temperature magmatic fluids. The findings highlight the importance of fluid chemistry and ligand availability in potentially modifying REE fractionation during post-orogenic hydrothermal alteration.

## 1. Introduction

The mobilization of rare earth elements (REE) within carbonate-rich hydrothermal environments is pivotal for the formation of Th–U–HREE mineral deposits in post-orogenic regions. Experimental and spectroscopic studies have demonstrated that carbonate and hydroxyl ligands can enhance REE solubility, particularly under moderately alkaline conditions (Migdisov and Williams-Jones, 2014; Louvel et al., 2022). However, the precise effects of temperature, pH, and ligand chemistry on LREE and HREE enrichment remain inadequately understood.

A recent study conducted in the Arıklı district (Biga Peninsula, NW Türkiye) identified dolomite-hosted Th–U–HREE mineralization and proposed that carbonate complexation is the primary mechanism for HREE transport (Tunc et al., 2025). Although the paragenetic findings are well documented, the geochemical analysis lacks the thermodynamic and fluid inclusion evidence necessary to substantiate the proposed model.

In this short communication, I reassess the geochemical feasibility of HREE mobilization in carbonate-rich hydrothermal systems using the Arıklı mineralization as a case study. By integrating existing experimental data and applying solubility-based constraints, I aim to elucidate the physicochemical conditions that facilitated HREE enrichment in these environments. The objective of this study is not to introduce novel datasets but to critically evaluate the geochemical boundaries and implications of existing experimental constraints when applied to a well-characterized carbonate-hosted REE system.

### 1.1. *Geological and metallogenic framework of the Arıklı mineralization (after Tunc et al., 2025)*

The Arıklı Th–U–REE mineralization, located in the Biga Peninsula of northwestern Türkiye, has been thoroughly documented by Tunc et al. (2025), who examined its geological setting, mineralogical characteristics and geochronological constraints. This mineralization is associated with dolomitized carbonate units and fracture systems that developed during Miocene extensional tectonics. Tunc et al. (2025) identified three mineralized zones within the Arıklı district. Zone B contains primary mineralization, characterized by fracture-controlled, HREE-rich assemblages within volcanic rocks. In contrast, Zones A and C, situated on either side of the central fracture system, are dominated by LREE-enriched mineralization in dolomitized carbonate rocks. This zonation is a significant geological feature of the Arıklı system and is essential for any proposed metallogenic models.

Based on mineral paragenesis, geochemical signatures, and cheralite U–Th–Pb ages of approximately 18 Ma, as reported by Tunc et al. (2025), a two-stage magmatic–hydrothermal model was proposed. Initially, high-temperature, mantle-derived alkaline magmatic fluids migrated along fracture systems, resulting in HREE-rich mineralization

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in Zone B. Subsequently, residual and cooling fluids permeated the surrounding carbonate host rocks, leading to LREE-dominant mineralization in Zones A and C during a lower-temperature phase of mineralization. This model effectively accounts for the observed spatial zonation and temporal relationship between magmatism, dolomitization, and REE mineralization in ore-bearing dolostone.

This study builds upon this geological framework by specifically examining the geochemical feasibility of alternative or overprinting fluid processes. Rather than replacing the magmatic–hydrothermal model of Tunc et al. (2025), this study evaluates whether low-temperature, carbonate-buffered hydrothermal fluids might have contributed to REE fractionation or alteration during late-stage fluid–rock interactions. By assessing the experimental and thermodynamic constraints on REE complexation, this reevaluation seeks to elucidate the potential influence and limitations of carbonate-rich fluids on the broader metallogenic evolution of the Arıklı system. Significantly, the magmatic–hydrothermal model proposed by Tunc et al. (2025) effectively accounts for both the primary source of rare earth elements (REE) and the primary spatial differentiation between the heavy rare earth element (HREE)-dominant Zone B and the light rare earth element (LREE)-dominant Zones A and C. This study does not aim to supplant this framework; rather, it seeks to assess whether late-stage, low-temperature fluid–rock interactions locally altered REE fractionation during the post-mineralization evolution of the system.

## 2. Geochemical constraints on HREE transport

Rare earth element (REE) mobility in hydrothermal systems is primarily governed by fluid composition, temperature, pH, and ligand chemistry. Experimental and spectroscopic studies have demonstrated that REE solubility can be enhanced in alkaline fluids through carbonate and hydroxyl complexation, with systematic differences observed between light and heavy REE as a function of temperature and ligand availability (Migdisov and Williams-Jones, 2014; Louvel et al., 2022). In general, the solubility of light REE (LREE) increases with temperature, whereas heavy REE (HREE) may be preferentially mobilized under moderate-to low-temperature conditions in fluids buffered by carbonate- and hydroxyl-bearing ligands. Recent thermodynamic models further suggest that alkaline, carbonate-buffered fluids provide favorable conditions for the stabilization of HREE-dominant aqueous complexes (Gysi et al., 2022). Complementary ligand-speciation studies indicate that $OH^-$, $CO_3^{2-}$, and, in some systems, $F^-$ complexes may act as important carriers of HREE in hydrothermal environments (Di and Ding, 2024).

The temperature–pH relationships discussed here are not derived from system-specific thermodynamic calculations for the Arıklı mineralization, but are instead used as illustrative constraints to evaluate the geochemical plausibility of late-stage HREE redistribution under carbonate-buffered conditions. Accordingly, these inferred conditions should be regarded as one of several plausible fluid scenarios rather than as a uniquely constrained representation of the mineralizing system.

Within this framework, a plausible interpretation for the Arıklı system is that moderately alkaline, carbonate-buffered hydrothermal fluids may have been capable of transporting HREE during dolomitization and subsequent cheralite precipitation. Such conditions would require pH values exceeding ~9-10 and temperatures in the range of approximately 120–180 °C, which are broadly compatible with the paragenetic sequence reported for the Arıklı mineralization. However, in the absence of system-specific thermodynamic modeling or fluid inclusion constraints, the precise physicochemical conditions governing HREE complexation and transport cannot be independently verified.

To illustrate these relationships, Fig. 1 presents modeled solubility trends for HREE and LREE as a function of temperature and pH in carbonate-buffered fluids. The shaded field represents the inferred range of physicochemical conditions considered plausible for late-stage fluid–rock interaction in the Arıklı system. These trends are consistent with predictions from recent experimental and thermodynamic studies (Gysi et al., 2022; Di and Ding, 2024), but are intended solely as conceptual constraints rather than as definitive system-specific models.

In carbonate-hosted hydrothermal systems, alternative ligands, such

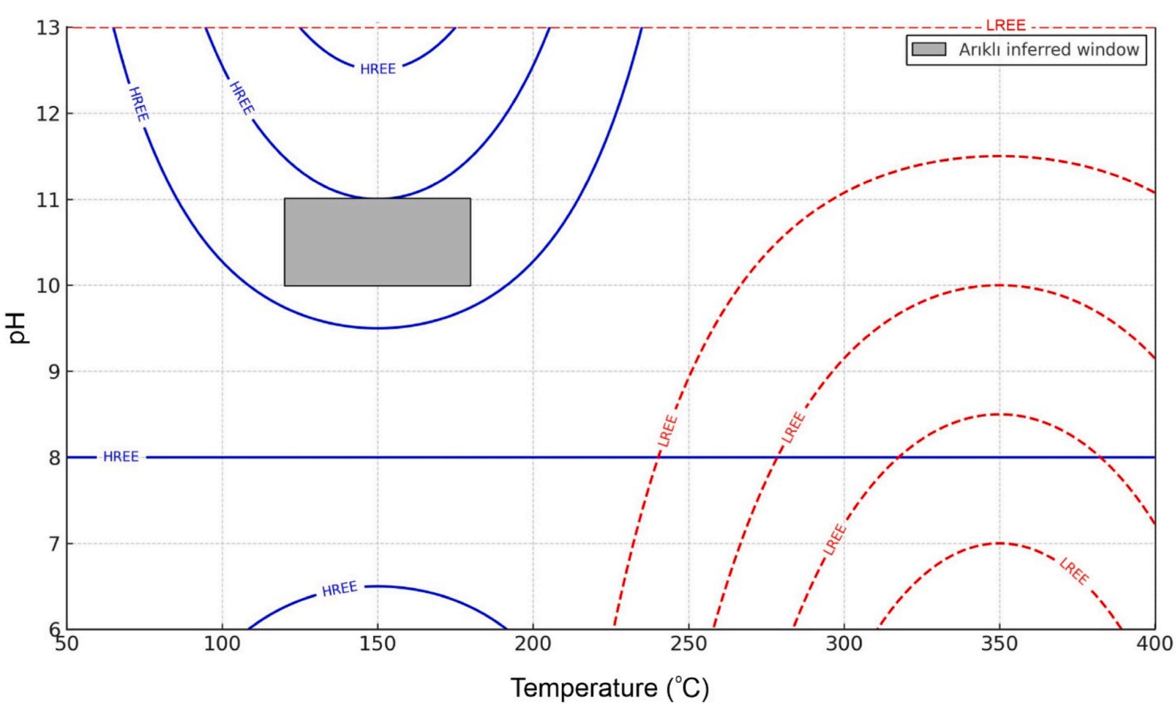


**Fig. 1.** Modeled solubility trends of HREE and LREE in carbonate-buffered alkaline hydrothermal fluids. Blue and red contours show contrasting solubility fields of HREE and LREE complexes, respectively. The shaded field marks the inferred temperature–pH window for the Arıklı system, consistent with enhanced HREE mobility (modified from Louvel et al., 2022; Gysi et al., 2022; Di and Ding, 2024). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

as sulfate, can significantly influence the speciation and fractionation of rare earth elements (REEs). In the absence of fluid inclusion microthermometry, Raman spectroscopy, or other independent methods to determine the overall fluid composition, it is challenging to ascertain the relative importance of complexation dominated by carbonate, hydroxyl, or sulfate in the Arıklı system.

In this theoretical model, the preferential accumulation of heavy rare earth elements (HREE) in Zone B may reflect localized fluid–rock interactions along structurally guided pathways, where conditions buffered by carbonates could have enhanced the complexation and transport of HREE. In contrast, the predominance of light rare earth element (LREE) signatures in Zones A and C might be attributed to lesser degrees of fluid–rock interaction or variations in ligand availability and fluid composition during the later stages of deposit development. However, without specific constraints on the sources and compositions of the fluids, these interpretations remain speculative and underscore the potential geochemical consequences of the proposed model.

## 3. Methodological reassessment of cheralite geochronology

Cheralite, a phosphate mineral containing thorium and uranium, is commonly associated with late-stage hydrothermal alterations and is increasingly employed for U–Th–Pb dating in low-temperature mineral environments. The reliability of cheralite geochronology is strongly influenced by the closure properties of the system and the potential incorporation of common lead. Experimental and microstructural evidence indicates that processes such as radiation damage, dissolution–reprecipitation, and fluid-assisted recrystallization can partially modify U–Th–Pb isotopic systems in both monazite and cheralite (Seydoux-Guillaume et al., 2002). As a result, the apparent ages often reflect hydrothermal overprinting rather than the timing of the original mineralization event.

In the case of the Arıklı mineralization, the approximately 18 Ma cheralite age corresponds to the Early Miocene extensional phase in northwest Türkiye, coinciding with dolomitization and regional alkaline magmatism. However, without in situ isotopic mapping or corrections for common lead, the precision of this age estimate remains uncertain. I suggest that combining Th–U–total Pb dating with textural and microchemical analyses (such as EPMA and LA-ICP-MS mapping) would provide a more robust understanding of the timing of cheralite formation and its relationship to fluid evolution.

## 4. Paragenetic and geochemical implications of dolomite evolution

In hydrothermal systems, multiple stages of dolomitization are frequently observed and are instrumental in regulating the transport and deposition of rare earth elements (REEs). The initial dolomite generation (D1) generally occurs under near-equilibrium conditions and acts as a passive host. In contrast, subsequent stages involved the formation of coarse, saddle-type dolomite (D2), indicative of renewed fluid flow and localized chemical exchange. Differences in texture, cathodoluminescence, and trace-element composition between these dolomite generations offer valuable insights into fluid evolution and metal-precipitation processes. In this context, dolomitization is primarily regarded as a chemical and pH buffer resulting from fluid–rock interaction, rather than as direct evidence of inherently carbonate-rich ore fluids. While progressive dolomitization may locally alter fluid chemistry and buffering capacity, it does not necessarily suggest that the mineralizing fluids were initially carbonate-dominated.

In the Arıklı system, two distinct dolomite generations are recognized: a fine-grained replacement dolomite that predates mineralization, and a coarse recrystallized dolomite associated with Th–U–HREE mineralization. Textural and isotopic contrasts between these generations indicate an episodic fluid regime characterized by progressive alkalinity increase and possible input of externally derived fluids. However, the absence of detailed microchemical data—such as variations in Sr–Mn–Fe or in-situ REE analyses—limits the precision of this interpretation. I suggest that future investigations integrating petrography with in-situ elemental mapping and carbonate clumped-isotope thermometry could provide a clearer understanding of the timing and sources of the fluids responsible for dolomite formation and associated mineralization.

## 5. Regional tectono-magmatic context and implications for fluid evolution

Magmatic activity during the Early to Middle Miocene in the Biga Peninsula and adjacent regions of northwestern Türkiye reflects a post-collisional extensional regime associated with lithospheric thinning following the closure of the northern branch of the Neotethys (Altunkaynak et al., 2012; Ersoy and Palmer, 2013). This geodynamic setting promoted widespread calc-alkaline to shoshonitic magmatism and associated hydrothermal circulation, providing favorable conditions for the development of Th–U–REE-bearing systems within both carbonate and volcanic host rocks.

Within this regional framework, the Arıklı mineralization is interpreted to have formed during Miocene extensional tectonics, when magmatically influenced fluids migrated through structurally controlled pathways and interacted with dolomitized carbonate sequences. Cheralite U–Th–Pb ages of approximately 18 Ma coincide with the peak of this magmatic activity, supporting a temporal link between magmatism, hydrothermal fluid circulation, and REE mineralization. As previously proposed, this tectono-magmatic context provides a robust explanation for the primary source of REE and the first-order spatial zonation observed in the Arıklı district.

In this study, the role of low-temperature hydrothermal fluids is considered within this broader geological framework. Rather than representing an independent ore-forming system, moderately alkaline, carbonate-buffered fluids are interpreted as potentially evolving from, or interacting with, magmatically influenced fluid systems during late-stage hydrothermal alteration. Such interactions may have contributed to localized REE redistribution or fractionation during dolomitization, without fundamentally controlling the primary metallogenic architecture of the system.

Accordingly, the regional tectono-magmatic setting supports a scenario in which late-stage, carbonate-buffered fluid–rock interaction operates as a secondary or overprinting process superimposed on an earlier magmatic–hydrothermal event. This perspective underscores the importance of integrating structural, paragenetic, and geochemical constraints when evaluating the role of fluid evolution in post-orogenic carbonate-hosted REE systems.

## 6. Conclusion

The re-evaluation of the Arıklı Th–U–HREE mineralization indicates that hydrothermal HREE enrichment in carbonate-hosted systems may be facilitated by the formation of stable carbonate–hydroxyl complexes at moderate temperatures (120–180 °C) and moderately alkaline pH (10–11) under specific conditions. This inferred thermodynamic window is consistent with experimental and thermodynamic studies that document the stability of HREE-dominant species under alkaline conditions (Louvel et al., 2022; Gysi et al., 2022; Di and Ding, 2024). Rather than providing a primary metallogenic explanation, the proposed solubility-based framework is intended to complement existing paragenetic interpretations by evaluating the potential role of late-stage carbonate-buffered fluid–rock interactions in modifying REE fractionation during dolomitization and hydrothermal alteration. Accordingly, this mechanism should be regarded as a secondary or overprinting process operating within a broader magmatic–hydrothermal system rather than a standalone model for REE mineralization. Future studies integrating fluid-inclusion constraints, system-specific thermodynamic modeling, and in situ isotopic analyses are essential to better quantify the role and limitations of such processes in post-orogenic carbonate-hosted REE systems.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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