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Review

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Review

Complexation of REE in Hydrothermal Fluids and Its Significance on REE Mineralization

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Abstract: Rare earth elements (REEs) have recently been classified as critical and strategic metals due to their importance in modern society. Research on the geochemical behaviors and mineralization of REEs not only provides essential guidance for mineral exploration but also holds great significance in enhancing our understanding of Earth's origin and evolution. This paper reviews recent research on the occurrence characteristics, deposit types, and hydrothermal behaviors of REEs, with a particular focus on comparing the complexation and transport of REEs by F, Cl, S, C, P, OH, and organic ligands in fluids. Due to the very weak hydrolysis of REE ions, they predominantly exist as either hydrated ions or free ions in low-temperature and acidic to weakly basic fluids. As the ligand activity increases, the general order of transporting REEs is $\text{Cl}^- \approx \text{SO}_4^{2-} > \text{F}^- \approx \text{PO}_4^{3-} > \text{CO}_3^{2-} > \text{OH}^-$ under acidic conditions or $\text{OH}^- > \text{SO}_4^{2-} \approx \text{Cl}^- > \text{F}^-$ under alkaline conditions. In acidic to neutral hydrothermal systems, the transport of REEs is primarily dominated by SO_4^{2-} and Cl^- ions while the deposition of REEs could be influenced by F^- , CO_3^{2-} , and PO_4^{3-} ions. In neutral to alkaline hydrothermal systems, REEs mainly exist in fluids as hydroxyl complexes or other ligand-bearing hydroxyl complexes. Additionally suggested are further comprehensive investigations that will fill significant gaps in our understanding of mechanisms governing the transport and enrichment of REEs in hydrothermal fluids.

Keywords: rare earth elements; REE; complexation; speciation; REE complex; hydrothermal fluids



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1. Introduction

Rare earth elements (REEs) are located in Group IIIB of the periodic table and consist of lanthanide, Sc (atomic number 39), and Y (atomic number 21) [1,2]. This series of elements can form stable +3 valence cations with similar ionic radii, resulting in similar physical and chemical properties and consistent geochemical behaviors during most geological activities [3–5].

In the modern world, REEs play an indispensable role in emerging technologies, green industries, and cutting-edge applications such as chemical catalysts, alloys, glass-polishing, aerospace technologies, permanent magnets, green energy production, national defense, and security [6–8]. These unique physical and chemical properties have earned them the moniker “The Vitamins of Modern Industry” [9–16]. Given their critical supply risk, irreplaceability, and substantial economic significance in modern technology sectors, worldwide recognition has led to REEs being included in the “Critical (Strategic) Raw Materials/Metals” catalogs by many countries for resource control purposes [17–22]. Consequently, research on the fundamental properties, mineralization, and mining applications of REEs has become a prominent topic [8,23–29].

Studying the fundamental properties of REEs is crucial not only for deciphering the evolution of Earth but also for providing theoretical insights into regional mineral exploration. Currently, evidence of fluid activity has been discovered in numerous rare earth and rare metal deposits [30–33]. Experimental studies further confirm that REEs could form stable complexes with various ligands in fluids (e.g., F^- , Cl^- , SO_4^{2-} , CO_3^{2-} , PO_4^{3-} and OH^-) and thus have the potential to be transported in the form of these complexes ([34] and references therein). In this paper, we provide a summary of recent experimental geochemical, geological, and thermodynamic research on REEs in different hydrothermal systems. This synthesis aims to offer theoretical insights into the hydrothermal geochemical behaviors of REEs during magma differentiation, hydrothermal alteration, and rock weathering to promote an understanding of REE mineralization.

2. Geochemical Character of REEs

REEs comprise a group of 17 elements, namely, La, Ce, Pr, Nd, Pm*, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Y, and Sc [2]. The geochemical behavior of REEs is quite similar, as they typically occur together in minerals with varying concentrations. Their comparable physical and chemical properties also pose challenges to the separation and purification processes of REEs [35]. Pm* stands out among the REEs due to its radioactive nature and lack of stable isotopes and has vanishingly small content in the crust [6,9,11,35]. Additionally, Sc shares many properties with REEs but is rarely coexistent with REEs in minerals. Moreover, Sc does not selectively combine with common ore-forming anions [36].

The abundance of different REEs in the crust exhibits significant variation. Generally, their abundance decreases with increases in their atomic number, as per the Oddo–Harkins rule which suggests that elements with even atomic numbers are more abundant than those with odd atomic numbers. Therefore, Ce stands out as the most abundant REE in the crust (Table 1), while Lu is particularly rare [8]. The ratio of light rare earth oxides to heavy rare earth oxides (LREO/HREO) in the crust is approximately 13:1 [11]. REEs in the crust are not low, with an average value of 63 ppm for Ce and 31 ppm for La, surpassing the average abundances of copper (28 ppm) and lead (17 ppm). Furthermore, Lu has an average crustal abundance of 0.31 ppm, much lower than that of most important metals but still higher than gold, silver, and platinum-group elements [37].

Table 1. Classification of REEs and average crustal abundances ¹.

Element	Atomic Number	IPUAC Classification	Average Crust (ppm) ²
La	57	Light	31
Ce	58	Light	63
Pr	59	Light	7.1
Nd	60	Light	27
Pm	61	Light	-
Sm	62	Light	4.7
Eu	63	Light	1
Gd	64	Light	4
Tb	65	Heavy	0.7
Dy	66	Heavy	3.9
Ho	67	Heavy	0.83
Er	68	Heavy	2.3

Table 1. Cont.

Element	Atomic Number	IPUAC Classification	Average Crust (ppm) ²
Tm	69	Heavy	0.3
Yb	70	Heavy	2
Lu	71	Heavy	0.31
Y	39	Heavy	39
Sc	21	None	14

- = Concentration too low to assess as a result of the short radioactive half-life of Pm. ¹ Adapted from [11] and [38]; ² According to [37].

Under specific conditions, some REEs can exhibit noticeable composition variations, such as significant negative anomalies observed in Eu and Ce under reduced and oxidized conditions, respectively [39–43], as well as REE fractionation driven by thermal diffusion [44–46]. REEs typically occur as trivalent cations. However, certain elements may also display alternative valent states; for instance, Eu and Yb can exist in a +2 valent state while Ce and Tb can occur in a +4 valent state (Figure 1). As the atomic number increases within the lanthanide series, there is a decrease in the ionic radii of REE ions due to what is known as “lanthanide contraction” [3,47]. This trend arises from the increased attraction between the nuclei of lanthanide elements and their respective 6s electrons. The enhanced attraction is not counterbalanced by additional electrons due to poor shielding properties exhibited by the 4f electrons [2,48].

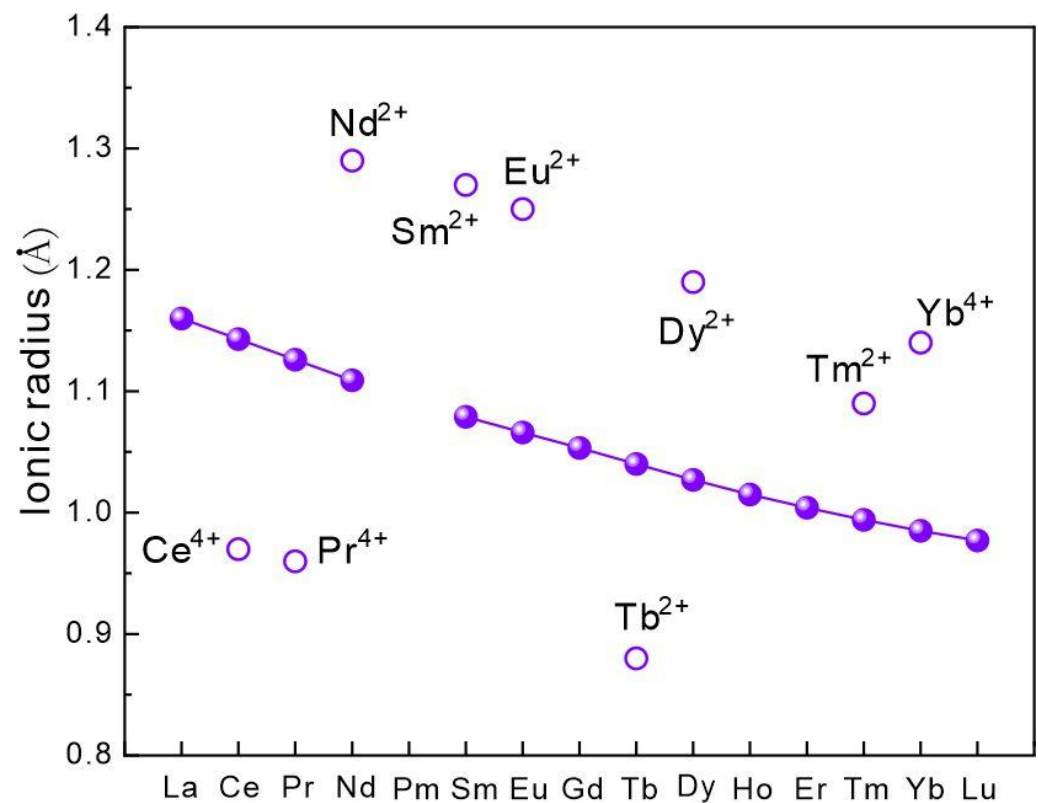


Figure 1. The ionic radius of REEs in VII coordination. The radius values are from Henderson (1984) [3].

3. Occurrence of REEs

Typically, REEs exhibit a high coordination number in minerals. For example, light REEs are commonly found in carbonates and phosphates with 8 to 10 coordination, while

heavy REEs are predominantly present as oxides or phosphate minerals with 6 to 8 coordination. Both LREEs and HREEs can also occur in silicate minerals [49–51]. On the other hand, Sc^{3+} in a VI coordination has a radius of approximately 0.75 Å, similar to Mg^{2+} (VI coordination: 0.72 Å) and Fe^{2+} (VI coordination: 0.78 Å), allowing them to readily substitute for Mg, Fe^{2+} , Zr, and Sn within lattices [2]. It is worth noting that pure metallic forms of REEs are rarely found in nature; instead, they typically exist as compounds or isomorphisms within minerals [35,52]. The ionic radius of trivalent REE cations ranges from approximately 0.86 Å to 1.03 Å in VI coordination, similar to those of Na^+ , Ca^{2+} , and Th^{4+} (VI coordination: 1.02 Å, 1.06 Å, and 1.15 Å, respectively) [13,49], which can enter minerals through isomorphism substitutions: $\text{Ca}^{2+} + (\text{Nb}, \text{Ta})^{5+} \leftrightarrow \text{REE}^{3+} + \text{Ti}^{4+}$ (titanates, niobates, and tantalates), $2\text{Ca}^{2+} \leftrightarrow \text{REE}^{3+} + \text{Na}^+$ (perovskite), $\text{REE}^{3+} + \text{Si}^{4+} \leftrightarrow \text{Ca}^{2+} + \text{P}^{5+}$ (apatite), $\text{Ca}^{2+} + \text{Th}^{4+} \leftrightarrow 2\text{REE}^{3+}$ (apatite), $\text{Ca}^{2+} + (\text{Al}, \text{Fe}^{3+}) \leftrightarrow \text{REE}^{3+} + \text{Fe}^{2+}$ (allanite), and $\text{Ca}^{2+} + \text{Si}^{4+} \leftrightarrow \text{REE}^{3+} + (\text{Al}, \text{Fe}^{3+})$ (garnet) [53–59].

HREEs are much less abundant than LREEs, primarily due to their lower concentration in Earth's crust [6,11,37,50,60]. Another contributing factor is that natural REE ores predominantly contain La, Ce, and Nd with a significantly lower proportion of HREEs [8,13]. The primary ore minerals for LREEs are monazite ((Ce, La, Nd, Th) PO_4) and bastnäsite ((Ce, La) $(\text{CO}_3)_2\text{F}$), while HREEs mainly originate from xenotime (YPO_4), apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$), eudialite ((Na, Ca, Ce) $_6(\text{Zr}, \text{Fe})_2\text{Si}_7(\text{O}, \text{OH}, \text{Cl})_{22}$), and ion adsorption clay deposits [6,9,12,61]. In addition to independent minerals, Sc often occurs in mafic minerals such as pyroxene and hornblende. Common Sc-containing minerals include thortveitite ($\text{Sc}_2\text{Si}_2\text{O}_7$), pretulite (ScPO_4), kolbeckite ($\text{ScPO}_4 \cdot 2\text{H}_2\text{O}$), jervisite ($\text{NaScSi}_2\text{O}_6$), and other minerals [62].

Nowadays, more than 270 different REE-bearing minerals have been identified [63], including bastnäsite, monazite, xenotime, allanite, pyrochlore, anatase, perovskite, ilmenite, rutile, and zircon (Table 2) [12,34,35,47,50,52,64–67]. As a result, silicate minerals account for approximately 43% of the total REE-bearing minerals, followed by carbonate minerals at 23%, oxide minerals at 14%, phosphate minerals at 14%, and other oxygen-containing salt minerals [9,11,47]. Except for xenotime, which is not influenced by crustal REE abundance, various REE-bearing minerals generally exhibit higher LREE contents compared to HREEs [68].

Table 2. REE-rich minerals and chemical formulas.

Mineral	Chemical Formula
Bastnäsite	(Ce, La, Nd, Y . . .) CO_3F
Parisite	$\text{Ce}_2\text{Ca} (\text{CO}_3)_3\text{F}_2$
Monazite	(Ce, La) PO_4
Xenotime	YPO_4
Fluocerite	(Ce, La) F_3
Eudialyte	$\text{Na}_4(\text{Ca}, \text{Ce})_2(\text{Fe}^{2+}, \text{Mn}^{2+}, \text{Y})\text{ZrSi}_8\text{O}_{22}(\text{OH}, \text{Cl})_2$
Pyrochlore	$(\text{Ca}, \text{Na}, \text{REE})_2\text{Nb}_2\text{O}_6(\text{OH}, \text{F})^1$
Vitusite	$\text{Na}_3(\text{Ce}, \text{La}, \text{Nd}) (\text{PO}_4)_2^1$
Fergusonite	$\text{Y} (\text{Nb}, \text{Ta}) \text{O}_3$
Perovskite	$(\text{Ca}, \text{REE}) \text{TiO}_3^1$
Ilmenite	$\text{Y}_2(\text{SiO}_4) (\text{CO}_3)$
Gadolinite	$(\text{Y}, \text{Ce})_2\text{Fe}^{2+}\text{Be}_2\text{Si}_2\text{O}_{10}$
Ancylite	$\text{Sr} (\text{Ce}, \text{La}) (\text{CO}_3)_2\text{OH} \cdot \text{H}_2\text{O}^1$
Apatite	$(\text{Ca}, \text{REE}, \text{Sr}, \text{Na}, \text{K})_3\text{Ca}_2(\text{PO}_4)_3(\text{F}, \text{OH})$

Table 2. Cont.

Mineral	Chemical Formula
Doverite	$\text{YCaF}(\text{CO}_3)_2$ ¹
Jervisite	$\text{NaScSi}_2\text{O}_6$
Kolbeckite	$\text{ScPO}_4 \cdot 2\text{H}_2\text{O}$
Pretulite	ScPO_4
Thortveitite	$\text{Sc}_2\text{Si}_2\text{O}_7$

¹ representative chemical formulas are provided here.

4. Types of REE Deposits

REE deposits can be classified into various categories based on their geological settings [8,10,50,69,70]. Recently, Goodenough et al. (2018) [8] divided REE ore deposits into two categories according to formation temperature [8]: (1) high-temperature REE deposits formed through magmatic and hydrothermal processes, commonly associated with carbonatite rocks, alkaline igneous rocks, and hydrothermal systems [63,71–80], where carbonatite-related REE deposits are the primary source of LREEs, accounting for approximately 51.4% of global rare earth oxide (REO) resources and 97% of China's rare earth resources [11,81]. The Bayan Obo and Maoniuping deposits in China are also the world's largest and third-largest rare earth deposits [30,82–85]; (2) low-temperature REE deposits formed by low-temperature processes, such as erosion and weathering. These include placer, bauxite, laterite, and ion adsorption clay deposits [8,11,12,50,63,86–90]. The ion adsorption clay deposits in South China are globally renowned for their significant contribution to the supply of HREEs [61,91–93].

Under the current REE supply system, LREEs primarily originate from REE deposits associated with carbonatite, while ion adsorption clay deposits in southern China are the dominant source of HREEs globally [60,94]. Carbonatites are igneous rocks composed of more than 50 vol% primary carbonate minerals such as calcite and dolomite [95] and exhibit the highest REE content among all igneous rocks [7,96]. The chondrite-normalized REE pattern in carbonatite demonstrates a remarkable enrichment of LREEs [7,78,97–99], which was likely achieved through (1) crystallization of primitive magma rich in REEs and (2) evolution of residual magma experiencing fluid activity in the late stage of magma [100–102]. The occurrence of abundant hydrothermal REE minerals (including barite, apatite, and fluorite, [81,88,103,104]) indicates significant hydrothermal activity in the Bayan Obo REE deposit. The hydrothermal processes are believed to play an important role during carbonatite REE mineralization [82,83,105]. Fluorine (F)- and phosphorus (P)-containing minerals like bastnäsite, xenotime, and monazite have also been discovered in other hydrothermal REE deposits [106,107]. The presence of these minerals indicates that F^- , SO_4^{2-} , and PO_4^{3-} in hydrothermal fluids play a crucial role in transporting and/or depositing REEs [67,108,109] during carbonatite-related REE mineralization.

The ion adsorption deposits in southern China have undergone a synergistic superposition of magmatism and weathering, which is well-documented. The granitic parent rocks, rich in REEs, underwent weathering, releasing REEs from minerals within the granites into the fluid phases. Subsequently, the REEs were adsorbed as ionic complexes by clay minerals present on the weathering crusts [61,89,110].

5. REE Complexes in Various Hydrothermal Fluids

Previous studies on natural samples from REE deposits, such as the Bayan Obo large REE deposit, the Dalucao breccia deposit, the Yinachang Fe–Cu–(REE) deposit, and the Sin Quden Iron Oxide–Copper–Gold (IOCG) deposit have provided evidence of fluid activities [30,32,33,83,98,107,111–118]. Zhang et al. (2022) [118] discovered high-density, CO_2 -rich, low-salinity (<5 wt.% $\text{NaCl}_{\text{equiv}}$) fluid inclusions in fluorite of the Dalucao breccia deposit. The fluid inclusions contain a significant amount of SO_4^{2-} along with small amounts of chloride (3.1%) and carbonate (4.4%) species. Therefore, SO_4^{2-} is believed

to transport REEs during the magmatic–hydrothermal stage. Xie et al. (2015) [119] analyzed fluid inclusions from the Maoniuping deposit and found that they contained up to 20 wt.% S and less than 1 wt.% Cl. Li and Zhou (2015) [31] discovered that fluids with varying compositions exert diverse effects on the mobility of REEs through fluorapatite geochemistry in the Yinachang deposit [31]. Fluid inclusions contain H_2O , CO_2 , alkali, and other ligands, including F^- , OH^- , Cl^- , SO_4^{2-} , CO_3^{2-} , and PO_4^{3-} [7,30,115,118].

Natural sample data, including fluid inclusions, have substantiated the presence of hydrothermal activity within REE deposits. Subsequent investigations have further confirmed the significant contribution of fluid activity in the transport and redistribution of REEs. Notably, in the Bayan Obo REE deposit, multiple phases of fluid activity have been identified, with fluids exerting a predominant influence on the redistribution and activation of REEs within minerals [116]. Similarly, in the Strange Lake REE–Zr deposit located in Canada, REEs were observed to transport alongside acidic fluids, with REE deposition and mineralization occurring as the fluid pH levels increased [120]. With advancing technology, an increasing number of studies such as in-situ XAS, Raman spectroscopy, and LA-ICP-MS on fluid inclusions have substantiated that fluid interaction plays a pivotal role in the genesis of REE deposits within carbonatite and alkaline igneous rocks [34,71,82,98,100,109,121–125]. The aforementioned research confirms that during magma evolution, hydrothermal fluids typically influence the activation and transport of REEs, while different aqueous ligands bind to REEs within melts or minerals, causing REE leaching from melt or mineral phases into fluids where they are transported as complexes [34,71,82,98,100,109,121–125]. These studies highlight the significant role of fluids in the activation, transport, and mineralization of REEs [87,126,127].

Turner et al. (1981) [128] investigated the hydrolysis behaviors of various elemental ions at $\text{pH} = 8.2$ and $I = 0.65$ (the value of ionic strength in mol/L), revealing that, except Sc, most REEs are resistant to hydrolysis at ambient temperature and can exist predominantly as ions in solution, while Sc exhibits partial hydrolysis [128] (Figure 2). Zero hydrolysis of most REE ions suggests that the predominant forms of REEs in solution are REE ions or hydrated ions in low-temperature and acidic to weakly basic fluids [34,61]. This could potentially serve as a crucial factor enabling REEs to form ion adsorption deposits.

Besides REE ions or hydrated ions, REEs can also exist as complexes, which could be dominated by the activity of ligands and the fluid's pH. Generally, with the ligand activity increasing, REE complexes prevail over hydrated ions. As pH increases, the hydrolysis of REEs intensifies, and REE–hydroxyl species dominate in solutions (Figure 3). Consequently, REE complexes might exert a significant influence on the transport of REEs during magmatic–hydrothermal processes.

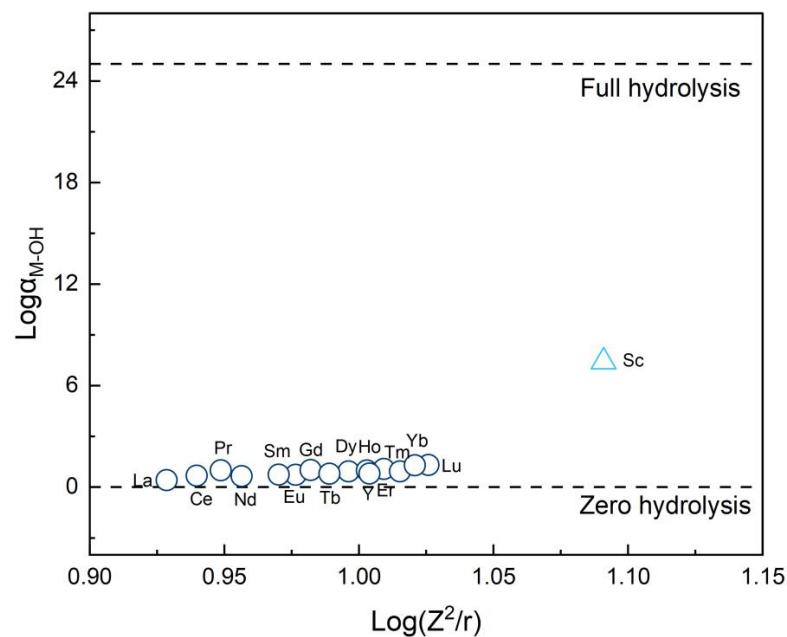


Figure 2. Plot of $\log \alpha_{M-OH}$ vs. $\log(z^2/r)$ for REE cations (3+) at 25 °C, pH = 8.2, and $I = 0.65$ suggesting that most REE ions hardly hydrolyze until the fluid's pH reaches 8.2, whereas Sc ions display weak hydrolysis behavior. $\log \alpha_{M-OH}$ represents the hydrolysis degree of REE ions following the reaction: $REE^{3+} + 3H_2O = REE(OH)_3 + 3H^+$, which is collected from [128]. $\log(z^2/r)$ stands for the strength degree of ionic polarization force, in which z is the valence state and r refers to the ionic radii [129]. Almost zero hydrolysis of most REE ions implies that REEs can exist in the form of REE ions or hydrated ions in low-temperature and acidic-weakly basic fluids.

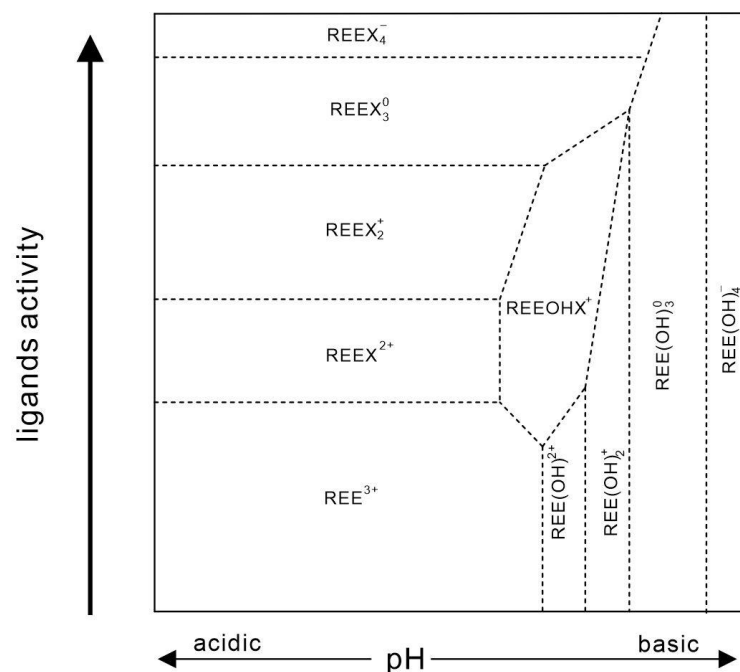


Figure 3. Model prediction illustrating the potential dominant species in fluids corresponding to the fluid's pH and the complexing ligand's activity based on the regular rules of ion complexation. X represents the ligand only, assuming its valence state is -1 . Because REEs display zero and weak hydrolysis, the stability fields of REE ions in fluids could be larger than those of most ore-forming metal ions, while the formation of the complexes would benefit from high complexing ligand activity.

According to the theory of “soft–hard acids and bases” [130], REEs are classified as hard acids and are expected to selectively bind with basic ligands such as F^- , SO_4^{2-} , CO_3^{2-} , PO_4^{3-} , and other hard base ligands [131]. Moreover, due to slight differences in atomic radii, the solubility of various REEs with the same ligands also varies [131–133]. Therefore, the stability of complex species significantly influences the presence of REEs in hydrothermal fluids.

High-temperature experiments conducted in the last century have postulated that REEs may predominantly exist as halogen complexes in hydrothermal solutions [134,135]. Theoretical predictions and thermodynamic experimental studies on REE-bearing solutions have confirmed that REEs can be transported and enriched in high-temperature fluids through complexation with ligands including F^- , Cl^- , PO_4^{3-} , SO_4^{2-} , CO_3^{2-} , and OH^- [34,54,108,109,131,133,136–141]. Among these ligands, Cl^- , F^- , and SO_4^{2-} have been further investigated for their roles in the transport and deposition of REEs [34,54,109,131,134–140,142–147]. Cl acts as a versatile base capable of forming diverse complexes with hard/soft acids, rendering REEs highly susceptible to the influence of high-salinity fluids [85,109]. Recent studies have shown that Na and K ions in fluids can also enhance the stability of REE complexes and enhance their transport capacity [99,148].

The research on the hydrothermal activity of REEs not only focuses on the species and stability of the complexes but also the solubility of REE-containing minerals [34,109,125,149]. However, due to the complex and diverse nature of these minerals, thermodynamic data has only been verified for a few fluorinated and phosphate minerals containing REEs (bastnasite, fluorite, xenotime) [34,68,109,131], while most other REE-containing minerals lack sufficient thermodynamic data.

5.1. REE Fluoride Complexes

Fluorite and F-containing carbonates, including bastnäsite and parisite, are commonly encountered in magmatic–hydrothermal REE deposits. IOCG deposits are also rich in REEs [106,112,150,151]. Considering the ability of F to form stable REE–F complexes [152–155], most studies suggest that the fluids associated with REE transport and mineralization primarily contain F. These studies explain the deposition mechanism of REEs in F-bearing fluids through three processes, namely, (1) the reaction between the mineralizing fluid and Ca-rich wall rock/fluid to generate low-solubility fluorite; (2) the defluorination of ore-forming fluid leading to a decrease in the activity of F in the fluid; and (3) the destruction of the stability of REE–F complexes [47,151,156,157].

Fluorine can decrease the solidus temperature and viscosity of silicate melts, as well as enhance ion diffusion rates [46,158–161]. Additionally, it can increase the solubility of minerals such as zircon, monazite, ilmenite, and rutile in fluids or melts [162–167]. This prevents REEs from being incorporated into these minerals and promotes their enrichment in residual melts [168]. However, recent findings by Duan et al. (2023) [169] suggest that F does not directly facilitate REE transport. Nevertheless, a high F content in magma could influence its crystallization history and result in REE enrichment followed by removal through exsolved volatiles.

Numerous studies have been conducted on the complexation and speciation of REEs in hydrothermal systems containing F [34,54,108,109,131,136,138,170–173], covering a temperature range from 5 °C to 500 °C. Based on the thermodynamic conclusions of [108], Luo and Miller (2004) [173] investigated the stability of $REEF^{2+}$ and $REEF_2^+$ complexes. Their results were consistent within the temperature range of 5–40 °C, with lower stability observed for LREE–F complexes compared to HREE–F complexes. Migdisov et al. (2009) [131] compared the first formation constants of REE–F and REE–Cl complexes based on their new experimental results [131] and discovered that at high temperatures, the stability of the LREE–F complex exceeded that of the HREE–F complex (Figure 4). They considered that the high-temperature data reported by [108] was extrapolated from ambient temperature rather than obtained through actual measurements at high temperatures. It is worth

noting that all these studies confirmed an increase in the stability of REE–F complexes as temperatures rise.

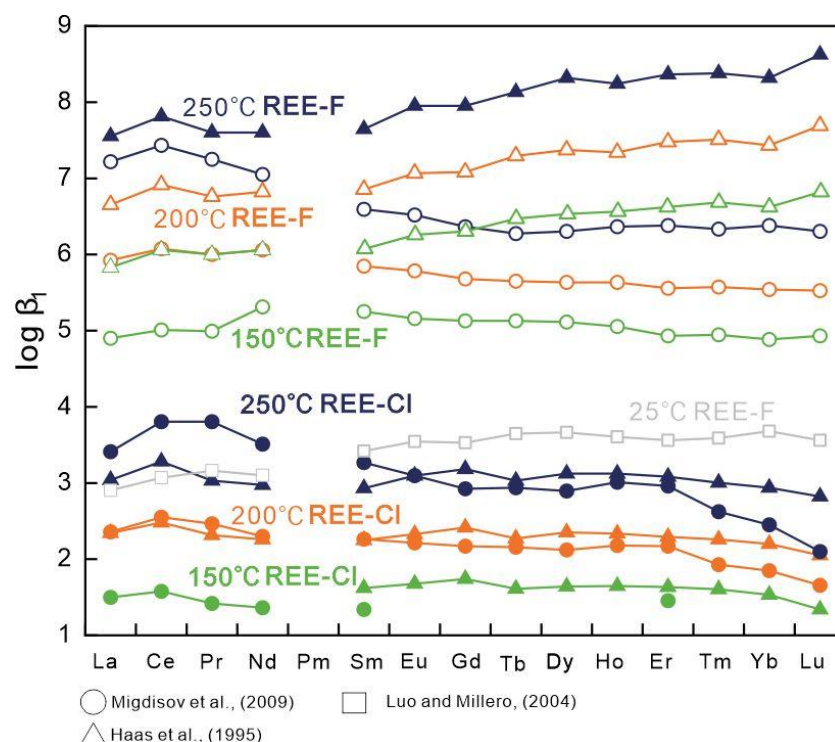


Figure 4. A comparison of the first formation constants of the complexes ($\text{REE}^{3+} + \text{F}^- = \text{REEF}^{2+}$; $\text{REE}^{3+} + \text{Cl}^- = \text{REECl}^{2+}$) shows that the stability of REE–F complexes is several orders of magnitude higher than that of REE–Cl complexes. The data are from [108,131,173].

In chloride–fluoride hydrothermal systems, Migdisov and Williams-Jones (2014) [109] discovered that, under acidic conditions, Nd primarily exists as NdCl_2^{2+} and NdCl_2^+ ; however, as the solution becomes neutral, the dominant species shifts to Nd–F complexes, resulting in a significant decrease in Nd concentration in the solution (<1 ppb) due to the precipitation of NdF_3 . On the other hand, under alkaline conditions, Nd predominately exists as $\text{Nd}(\text{OH})_3^0$ and $\text{Nd}(\text{OH})_2^+$. With increasing temperature, there is an intensified complexation of Nd with chloride and a gradual increase in the pH boundary for both Nd–chloride and Nd–fluoride from 3.5 at 200 °C to 4 at 300 °C and to 6.4 at 400 °C. It can be observed that low-temperature and neutral conditions are favorable for the formation of Nd–fluoride complexes. However, due to its low solubility in F-containing solutions, the transport of Nd by such solutions is limited. In addition, the complex forms of Ce (representing LREE) and Er (representing HREE) are similar to those of Nd under different conditions [109]. Although aqueous REE–fluoride complexes (REEF^{2+} and REEF_2^+) exhibit remarkable stability at ambient temperature [131], thermodynamic models suggest that the solubility of these complexes is relatively low at higher pH levels. Furthermore, at lower pH levels, the solution activity of REE–fluoride complexes also decreases, resulting in hindrances and reduced efficiency in transporting REEs in F-containing hydrothermal at any stage. Hence, it is speculated that F is more likely to serve as the primary binding ligand for depositing REEs [109,133].

According to the above geochemical studies, it is proposed that REE–F complexes are not the primary form of REE transport. This belief stems from several key factors. Firstly, HF^0 usually displays weak ionization, resulting in a limited release of F^- ions for complexing metal anions [174,175]. During geological processes, hydrothermal fluids containing REE are typically acidic to neutral, which compresses the stability range of REE–F [34,117]. Similarly, Cl is widely present in hydrothermal settings as an anionic

ligand with an average content of 10 wt.% [109], while F is mostly present in ppm levels in solution, except for abnormal enrichment [72]. Moreover, high temperatures further inhibit its ionization process, such that F- only exists in abundance under neutral to weakly alkalic conditions [133,176]. Secondly, the favorable pH range for transporting REEs closely aligns with that required for REEF₃ precipitation, resulting in low levels of soluble REEs [109]. Lastly, the solubility product of REEF₃ is much lower than that of REECl₃ [109]. Consequently, as fluoride content increases, it may even decrease the concentration of dissolved REEs [138].

At present, research is scarce on Yttrium. Loges et al. (2013) [177] experimentally demonstrated that in aqueous solutions containing F, yttrium exhibits a higher degree of fluorination. At temperatures ranging from 100 to 250 °C with fluoride concentrations between 1 and 330 mmol/L, YF₂⁺ predominates significantly over YF²⁺.

5.2. REE Chloride Complex

In carbonatite and alkaline igneous REE deposits, Cl[−] and SO₄^{2−} are commonly found as ligands in fluids [33,127]. Recent studies have confirmed the important role of chloride complexes in transporting REEs. Fluid inclusion data suggests that ore-forming fluids exhibit high salinity (32%~37% NaCl_{eqv}) and low pH, indicating that REEs may exist in the form of chloride complexes (Jbel Boho LREE vein, Morocco) [178]. Furthermore, chlorine has been identified as a primary ligand for transporting REEs based on studies conducted on the Dalucao brecciated ore REE deposit in China and the Sin Quye hydrothermal IOCG REE deposit in Vietnam, where it was observed to be present in numerous fluorite fluid inclusions [33,115]. Experimental studies on metal fluid/melt transport have also shown that the partition coefficient ($D_{\text{fluid/melt}}$) of REEs increases with chloride content in fluids [179]. Payne et al. (2023) [180] conducted fluorite solubility and REE transport experiments at different pHs, salinities, and temperatures. The experiments showed that adding NaCl can enhance the solubility of REEs in base solutions, with concentrations in the fluid reaching similar levels to the acidic solutions (i.e., NaCl-free and NaCl solutions). In the simulation study of complex species, it was also found that variations in pH and ligands lead to distinct dominant species of REE in the solution [34,180].

Louvel et al. (2015) employed XAS (X-ray absorption) to investigate the solubility of Yb and observed that under hydrothermal conditions with pH < 2 and NaCl_{eqv} > 5 wt.%, the formation of aqueous REE complexes was favored, resulting in a significant increase in Yb solubility ($\approx n \times 1000$ ppm) [181]. Studies also indicate that chloride occurs predominantly as REECl²⁺ and REECl₂⁺ in fluids [34]. Migdisov and Williams-Jones (2014) [109] conducted experiments to analyze Nd complex species in solutions containing chloride, revealing that a NaCl solution with a concentration of 10 wt.% at various temperatures could transport 200 ppm of Nd within a high pH range (pH = ~ 5). The stability of REE–Cl complexes decreases with increasing atomic numbers at elevated temperatures (Figure 4). Therefore, LREEs, compared to HREEs, is more susceptible to being transported by Cl[−].

At low pH and high temperatures, HF exhibits weaker ionization compared to HCl and predominantly exists in the form of HF⁰ in the fluid [47,174,175], while chlorine mostly exists as Cl[−]. Thermodynamic simulation and hydrothermal experiments demonstrate that the stability of LREE–chloride complexes at high temperatures is higher than previously expected, whereas the stability of HREE–chloride complexes is overestimated (Figure 4) [34,108]. In comparison to the solubility of REEF₃, REECl₃ exhibits higher solubility, indicating a stronger ability for chloride to transport REEs. As a result, chlorine may serve as the primary ligand for REE transport and enrichment in hydrothermal fluids [34,176].

5.3. REE Sulfate Complex

Previous studies have demonstrated that SO₄^{2−} could serve as a ligand for the transport of REEs during the magmatic–hydrothermal process [85,127,181–186], and it has been identified in various deposits, such as the Yinachang Fe–Cu–(REE) deposit and Dalucao breccia deposit. A compositional analysis of hydrothermal fluids from the Mutnovsky

volcano in the Kamchatka area reveals that an increase in pH ($\text{pH} < 6$) leads to a decrease in REE concentration within hydrothermal systems. Particularly, acidic hydrothermal fluids containing SO_4^{2-} exhibit significantly higher ΣREE concentrations compared to alkaline hydrothermal fluids containing CO_3^{2-} [187], suggesting that SO_4^{2-} is more favorable to REE dissolution and transport compared to CO_3^{2-} . Similarly, in carbonatite systems, sulfate (SO_4^{2-}) proves to be more effective than Cl^- for transporting REEs due to its greater formation constant for REE-SO_4^{2-} complexes (Figures 4 and 5). Moreover, numerous species of polynuclear complex elements associated with REE-SO_4^{2-} complexes may possess stronger capabilities for transporting REEs [34,141,147,188,189]. Other experimental studies have also highlighted the significance of the REE-SO_4^{2-} complex in facilitating the transport of REEs under high-temperature conditions and weakly acidic to near-neutral pH levels [109,139]. Therefore, sulfate is widely recognized as a crucial complexing agent for facilitating the transport of REEs within hydrothermal systems [109,119].

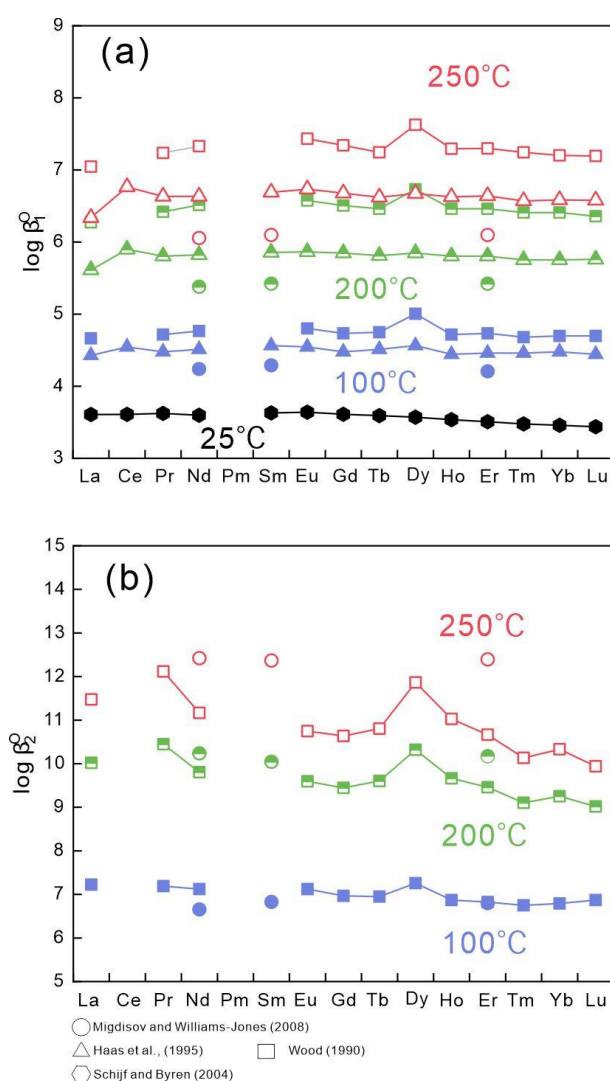


Figure 5. Comparison of the first (a) and second (b) formation constants of REE-SO_4^{2-} complexes suggesting that elevated temperature facilitates the formation of REESO_4^+ and $\text{REE}(\text{SO}_4)_2^-$ complexes and that the stability of $\text{REE}(\text{SO}_4)_2^-$ species is higher than that of REESO_4^+ at similar temperatures. The data from [54,108,139,190].

Determining the formation constants of REESO_4^+ and $\text{REE}(\text{SO}_4)_2^-$ complexes is important for comprehending the transport and enrichment of REEs in hydrothermal fluids

containing sulfates [54,136,139,190]. Previous studies have demonstrated that the stability of REESO_4^+ at high temperatures, as reported by [108] and [136], exceeds the calculated values provided by [139]. Although there was a minor discrepancy between these two datasets at ambient temperature, this difference becomes more pronounced with increasing temperatures (Figure 5). While not explicitly discussed by [139], previous research on chloride and fluoride complexes suggests that this phenomenon may be attributed to variations in HKF parameters (e.g., G : Gibbs free energy, α : activity). At ambient temperature, the stability of the REESO_4^+ complex slightly decreases with the atomic number [190]; however, this variation among elements is even smaller than the calculation uncertainty. Migdisov et al. (2016) [34] proposed that this insignificant difference has less impact on the stability of the REESO_4^+ complex at high temperatures since temperature escalation does not significantly alter its stability [34].

In high-temperature hydrothermal fluids, REEs mainly exist in the form of $\text{REE}(\text{SO}_4)_2^-$ complexes, while the abundance of mono-sulfate REESO_4^+ complexes is relatively low [109]. Experimental studies have indicated that REE-SO_4^{2-} complexes play a significant role in saturated aqueous solutions containing quartz due to REEs' close association with SO_4^{2-} ions [189], which can be attributed to the breakdown of SiO_2 at high temperatures facilitating sulfate dissolution and enhancing the binding between REEs and SO_4^{2-} ions. Rudolph and Irmer (2015) [191] confirmed the presence of LaSO_4^+ in a solution at 100 °C through in situ Raman observation, although $\text{La}(\text{SO}_4)_2^-$ was not detected. Wan observed diverse complex forms of REE-SO_4^{2-} at high temperatures including $\text{REE}(\text{SO}_4)_2^-$ and REESO_4^+ , as well as REE-HSO_4^{2-} and other polynuclear complexes, inferring that the REE-HSO_4^{2-} and polynuclear complexes may play a more significant role in transporting REEs [147]. Furthermore, under high pressures and temperatures, there is a substantial increase in the solubility of REEs in sulfate-containing solutions [141].

Migdisov and Williams-Jones (2014) [109] conducted experiments on the complexation of Nd in a chloride–sulfate solution and determined that $\text{Nd}(\text{OH})_3$ was the sole solid precipitate formed. The pH range of Nd transport in the solution is wide (400 °C, $\text{pH} < 7.5$), exceeding that observed in solutions containing only chloride ($\text{pH} < 5$). Furthermore, the prevalence of REE-Cl complexes is limited to low-pH acidic conditions (300 °C, $\text{pH} < 2$). Migdisov et al. (2016) [34] consider that the enhanced transport capability of SO_4^{2-} can be attributed to its approximately 2.5–3.5 orders of magnitude higher stability compared to REE-Cl complexes; however, there is currently no definitive explanation for the predominance of REE-Cl complexes under strongly acidic conditions. In summary, it can be confirmed that SO_4^{2-} can act as a transporting ligand for REEs.

5.4. REE Carbonate Complexes

Carbonates are considered to be a significant phase for incorporating REEs, and the ability of CO_3^{2-} to transport REEs has become a prominent research topic in recent years [30,32,76,79,83,192]. The enrichment of REEs and thorium in carbonatites is often associated with hydrothermal activity [71,82,100,122,193]. Under ambient conditions, carbonate complexes are highly stable [192,194,195]. Cantrell and Byrne (1987) [194] confirmed that REECO_3^+ and $\text{REE}(\text{CO}_3)_2^-$ are the primary aqueous complexes of REEs in seawater, with LREEs being preferentially associated with REECO_3^+ and HREEs preferentially associated with $\text{REE}(\text{CO}_3)_2^-$.

Previous thermodynamic predictions suggest that the stability of REE-carbonate complexes at temperatures up to 300 °C is comparable to those of REE-fluoride complexes [108,136]. However, Migdisov et al. (2016) [34] utilized extrapolated thermodynamic data on Eu–carbonate from previous studies and observed significant variations in values predicted by different researchers at different temperatures, indicating a serious lack of thermodynamic data for REE-CO_3^{2-} complexes [34]. By comparing the formation constants of REE-F complexes and REE-CO_3^{2-} complexes, it was found that the first formation constants for Eu– CO_3^{2-} complexes were higher than those for Eu–F complexes (Figures 4 and 6), indicating that the stability of REE-CO_3^{2-} complexes is greater than that of REE-F . Nonetheless, this data solely represents predicted

values under standard conditions, with discrepancies in high-temperature environments. Zhang et al. (2023) [85] discovered a large number of fluocerites from the Taipingzhen deposit during an early high-temperature hydrothermal stage. The study shows that earlier-formed fluocerites should be supplanted by later-formed bastnaesite. It was revealed that continuous exposure to high temperatures resulted in CO₂ release and the preservation of fluocerite, whereas, when temperature declined slowly, bastnaesite replaced fluocerite. Therefore, it can be predicted that the stability of REE–F complexes is greater than that of REE–CO₃^{2−} complexes at high temperatures.

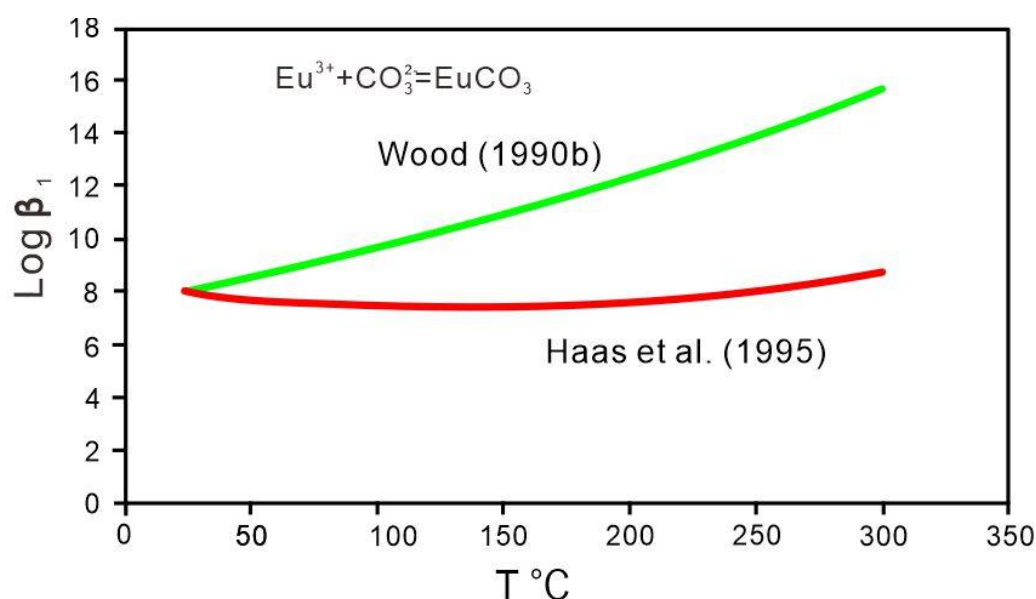


Figure 6. The values for the first formation constants of Eu–CO₃^{2−} [108,136].

In neutral fluids containing carbonate, REEs primarily exist in the form of carbonate complexes (HCO₃[−] and/or CO₃^{2−}). However, under acidic conditions, the presence of carbonate complexes in solutions may be negligible, as mentioned by [196]. The high halogen content in hydrothermal systems could limit the formation of REE–CO₃^{2−} complexes. Other studies have suggested that in low-salinity fluids rich in CO₂, REEs can form complexes with CO₃^{2−}; in high salinity systems abundant in CO₂, REEs may be transported in the form of chlorine or sulfate complexes; and in alkaline fluids, REEs might occur in the form of REE–OH complexes [149]. Moreover, the solubilities of solid minerals corresponding to REE–CO₃^{2−} complexes are also low, suggesting that the effect of carbonate on transporting REEs in solutions may be minimal. However, recent research by [148] has shown that hydroxyl carbonate complexes can enhance the hydrothermal mobilization of REEs under alkaline conditions (LREE: >300 °C; HREE: <300 °C), which might be the main mechanism for redistributing REEs within carbonatite rocks [197]. The depletion of LREEs in hydrothermal fluids related to carbonatites in the Kamtai area may also be attributed to this mechanism. Moreover, fluid inclusion analysis of the Strange Lake (Canada) REE deposit reveals a pH variation for the ore-forming fluids, ranging from alkaline conditions (425 °C, pH ~ 10) to acidic conditions (300 °C, pH ~ 3) [124]. In alkaline solutions, HCO₃[−] was considered a complexing agent for REEs due to charge balance considerations, abundant carbonic inclusions, and the presence of nahcolite. Additionally, based on experimental evidence [198], hydroxyl carbonate is also recognized as an important carrier of REEs, particularly in alkaline fluids. Fractional crystallization of carbonatite magma could lead to alkali enrichment in solutions [16,199–201], creating a favorable environment for the formation of alkaline hydrothermal fluids that potentially transport REEs through CO₃^{2−}.

5.5. REE Phosphate Complexes

Previous studies have suggested that the transport of REEs can be influenced by phosphate, and REEs may be transported in the form of phosphate complexes or in conjunction with other ligands. However, in hydrothermal systems rich in fluorine and phosphorus, it is challenging to extensively transport REEs [202], suggesting that phosphorus may play a similar role to F in transporting and depositing REEs. The remarkably low solubility of REE phosphate minerals (monazite and xenotime) also limits the amount of transferable REEs in fluids [75], making it unlikely for PO_4^{3-} to significantly impact REE transport [47]. Gysi studied the species of REE–phosphate/chlorine complexes and found that the content of soluble REEs in the H_3PO_4 system was minimal, whereas the total amount of soluble REEs in the HCl system was 2–4 orders of magnitude higher compared to the H_3PO_4 system when conducting experiments involving H_3PO_4 –HCl–HF [203]. This suggests that the formation of REE–Cl complexes dominates REE transport, comparable to REE–F and REE– PO_4^{3-} complexes.

The experimental investigation of the REE– PO_4^{3-} complex further confirms that phosphate acts as the ligand for the deposition of REEs and has limited transport ability towards REEs. In natural hydrothermal systems with multiple ligands, REEs are often observed to be transported along with Cl^- or SO_4^{2-} , and subsequently precipitate with F^- , CO_3^{2-} , and PO_4^{3-} . However, the thermodynamic data regarding the REE– PO_4^{3-} complex and related minerals primarily rely on the theoretical predictions of [108], which also require additional thermodynamic data for supplementation.

5.6. REE Hydroxyl Complexes

REEs can also exist as hydroxyl complexes in hydrothermal solutions, such as $\text{REE}(\text{OH})_3^0$, $\text{REE}(\text{OH})_2^+$, and $\text{REE}(\text{OH})^{2+}$ [204,205]. However, the only experimental study on the stability of REE–OH complexes to date was conducted by [142]. In comparison with theoretical calculations [108], the pH dominance range of Nd^{3+} at 290 °C is significantly broader. The contribution of $\text{Nd}(\text{OH})_2^+$ to the dissolution of Nd is slightly reduced, and the dominance range of $\text{Nd}(\text{OH})_2^+$ is smaller than predicted, whereas under basic conditions, $\text{Nd}(\text{OH})_3^0$ prevails more commonly [34] (Figure 7).

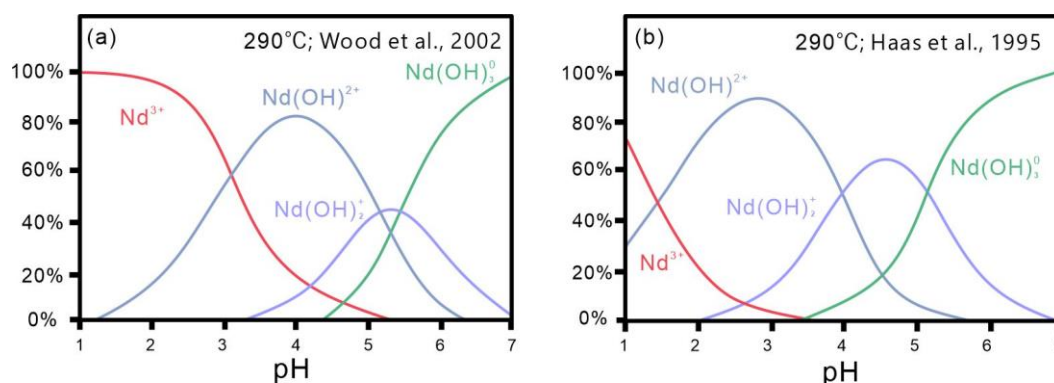


Figure 7. The relationship between dominant Nd species and pH is based on thermodynamic data at 290 °C [108,136]. Under acidic conditions (pH < 2), Nd mainly exists in the form of Nd^{3+} (a), while in neutral to base conditions (pH = 3–5), $\text{Nd}(\text{OH})_2^+$ and $\text{Nd}(\text{OH})_3^0$ are mainly dominated (b). Data from [108,142].

5.7. REE Organic Complexes

Lecumberri-Sanchez et al. (2018) [206] discovered a significant concentration of REEs in oil-bearing low-temperature basin brine ($\sum \text{REE} > 1000 \times n$ ppm) within the El Hammam Fluorite Mining Area, Morocco. They hypothesized that the enrichment of REEs in this region could be attributed to transportation facilitated by acetic acid complexes. Given

the diverse range of organic compounds present, investigating the stability of REE complexes associated with these compounds appears feasible. However, dealing with such complex systems poses a considerable challenge due to their distinct properties. Furthermore, organic compounds often exhibit property changes at high temperatures, further complicating research efforts.

6. Geological Implications

The requirement for achieving REE enrichment at the ore-forming level is that the parent magma must contain a sufficient amount of REEs and undergo further enrichment through magma evolution. This process is influenced by factors such as the oxidation state of the magma, differentiation during crystallization, and enrichment in alkali elements [207–211]. Carbonatite and alkaline magmas may contain various volatile components, including CO_2 , H_2O , Cl, F, and S [7,78,97–99]. As crystallization progresses, these components, along with various incompatible elements, accumulate in residual magma. They can then fractionate into separate fluid phases. The presence of fluid inclusions and evidence of alkaline metasomatism provide clear indications for the separation of volatile fluid phases [30,83,115]. Depending on the composition and evolution of the magma, the main minerals containing REEs can either crystallize directly from the magma, such as bastnäsite in the Mountain Pass deposit, or REEs can exist as an incompatible element in residual magma and be carried and distributed into the fluid phase by the exsolution fluids. The exsolution of the fluid phase from the melt is influenced not only by the composition of the melt but also by changes in temperature and pressure [7]. In high-temperature and high-pressure fluids, due to the enhanced hydrolysis of REEs, the dominant species of REE could change from simple hydrated ions to REE–ligand complexes [34,212]. Therefore, in the high-temperature environment of magmatic systems, the most influential factors on the transport of REE are often various ligands. These ligands play a vital role in facilitating the distribution of REEs within both magmatic and hydrothermal systems.

In acidic–neutral hydrothermal systems, the transport of REEs is primarily controlled by SO_4^{2-} and Cl^- ions, while the presence of F^- , CO_3^{2-} , and PO_4^{3-} ions play a crucial role in the deposition of REEs [34,109,121,139,180,213]. In alkaline hydrothermal systems, REEs mainly exist in solutions as hydroxyl complexes [181]. Additionally, in neutral to alkaline solutions, the formation of hydroxyl carbonate complexes becomes increasingly significant for REE deposition [148,149,181,198,204].

To further investigate the disparity in the transportability of REEs by Cl and F, the ionization constants were utilized to calculate their respective ionization and transport quantities. Figure 8 illustrates that REE–F complexes exhibit lower transport ability compared to REE–Cl complexes. Consequently, it can be inferred that chloride ions (Cl^-) should also serve as the preferred ligand for transporting REEs.

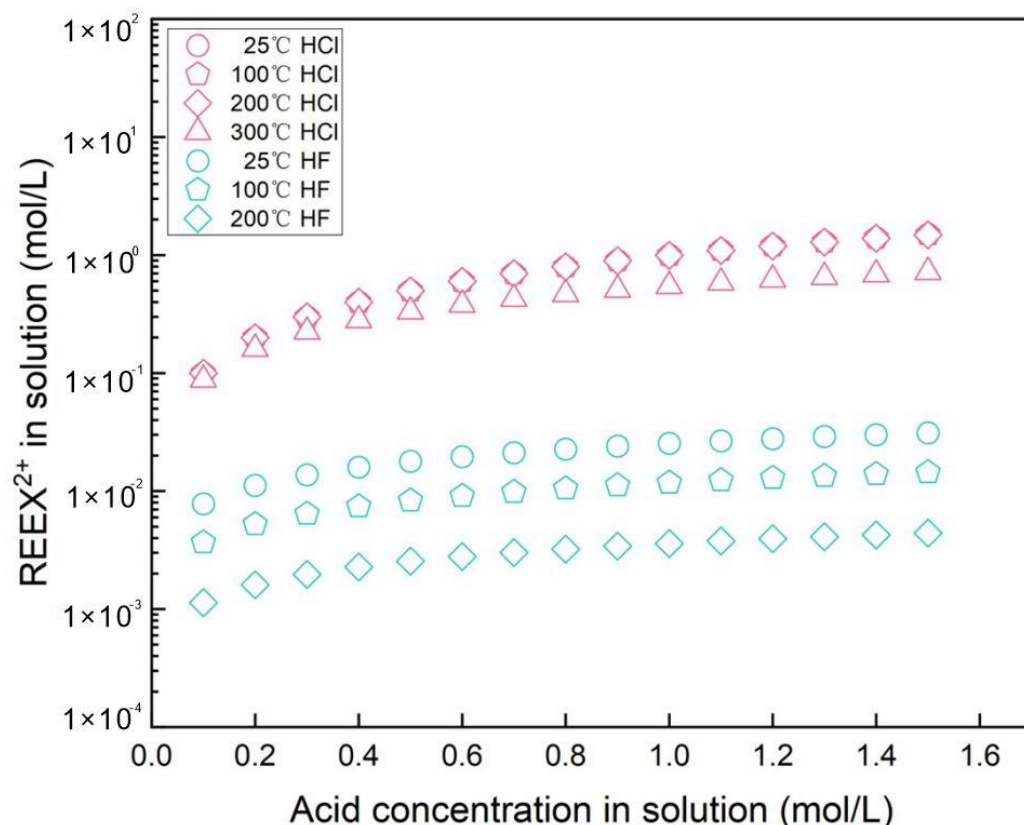


Figure 8. The model calculation reveals comparable transport capacity between the REEF^{2+} complex and REECl^{2+} complex based on the ionization equilibrium constant (K) of HCl and HF. Note that HCl is highly ionized below 200 °C. The $\log(K_{\text{HF}})$ used to calculate is -3.18 at 25 °C, -3.85 at 100 °C, and -4.89 at 200 °C [214], while $\log(K_{\text{HCl}})$ is 6.79 at 25 °C, 4.6 at 100 °C, 2.16 at 200 °C, and -0.18 at 300 °C [215].

As previously mentioned, the hydrolysis of REEs increases with rising temperature and pH levels. Consequently, at elevated temperatures, the transportation of REEs is predominantly governed by the presence of dominant complex species (Figures 2 and 3). However, as the temperature drops or pH decreases, REEs gradually exist in the solution primarily as REE^{3+} ions. Therefore, in low-temperature deposits, REE^{3+} ions are carried by fluids and subsequently absorbed by clay minerals within weathered clay zones. In hydrothermal deposits hosted in carbonatites and alkaline igneous rocks, REEs are transported as complexes and subsequently deposited as minerals. In geological processes, hydrothermal fluids often contain high concentrations of F^- ions [215] and/or other ligands [33,115,178]. Additionally, fluid inclusion analyses commonly reveal the presence of substances such as SO_4^{2-} , CO_3^{2-} , and PO_4^{3-} ions [82,85,100,127,182–186,193,202]. Based on available data, the transport abilities of different ligands for REEs follow the order, at high temperature ($T > 300$ °C) and the same concentration (assuming the average content of chlorine of ~ 2.5 mol/L): $\text{Cl}^- \approx \text{SO}_4^{2-} > \text{F}^- \approx \text{PO}_4^{3-} > \text{CO}_3^{2-} > \text{OH}^-$ (under acidic conditions); $\text{OH}^- > \text{SO}_4^{2-} \approx \text{Cl}^- > \text{F}^-$ (under alkaline conditions) [34]. In this scenario, $\text{REE-CO}_3^{2-}\text{-OH}$ complexes may exhibit greater transport abilities for REEs under alkaline conditions. It is important to note that this order applies only to strong acidic or strong alkaline conditions. The effects of temperature, pH, and ligand concentration on this order should not be overlooked, and specific circumstances require individual analysis.

7. Prospects for Future Research

There are still significant gaps in our understanding of the mechanisms governing the transport and enrichment of REEs in hydrothermal fluids. For instance, there remains a

lack of knowledge regarding the complex species formed by REEs under high temperature and pressure conditions. As shown in Figure 3, there could be diverse potential dominant species in fluids corresponding to the fluid's pH and the complexing ligand's activity in theory; however, only a few have been confirmed so far. Additionally, the formation constants for REE complexes are insufficiently characterized, as are the thermodynamic parameters associated with REE minerals. Furthermore, further investigation is needed to elucidate the relationship between K/Na ratios and REE complexes, as well as how ambient conditions influence these complexes.

The study by Migdisov and Williams-Jones (2014) [109] is also based on the experimental findings of Banks et al. (1994) [182]. Although the overall conditions in these studies are relatively ideal, practical scenarios may involve additional factors that could influence the presence of HF in solutions and the formation of REE–F complexes. In geological processes, ore-forming fluids with high HF contents are commonly encountered [72,216]. However, it is still necessary to supplement new experimental data to determine whether higher coordinated REE–F complexes exist under high temperature and pressure conditions and establish thermodynamic data for REE–F complexes at elevated temperatures.

The experimental studies on sulfate systems indicate that sulfate is a key ligand for transporting REEs in hydrothermal solutions, leading to the mobility of a significant amount of REEs. However, it remains unclear which complex species enable the most efficient transport for REEs. Moreover, research on the complex species at temperatures exceeding 400 °C has yet to be conducted. Conclusions regarding the formation constants of REE–sulfate complexes are based on the experimental data, which indicates that REE–SO₄^{2−} complexes remain stable at temperatures above 250 °C. Nevertheless, these findings may have limitations, and further research is necessary to gain deeper insights into the transport behavior of REEs in sulfate systems at high temperatures.

The transport capacity of REE–chloride complexes is not internally restricted, unlike systems containing fluorine. This suggests that Cl can effectively transport significant amounts of REEs under specific pH conditions in natural hydrothermal systems. Recent research on the transport of chlorine in REEs has demonstrated that REEs can be transported as chloride complexes (NdCl²⁺ and NdCl₂⁺) within hydrothermal systems [34]. The transport potential of Cl in transporting REEs is substantial, making it an essential ligand for REEs in hydrothermal processes. Therefore, future research should focus primarily on exploring variations in partitioning coefficients of REEs in chloride-containing hydrothermal fluids across different systems, temperatures, and pressures to understand factors contributing to the selective enrichment of REEs during magmatic–hydrothermal or fluid activity stages.

The aforementioned studies on REE–CO₃^{2−} /REE–PO₄^{3−} complexes are primarily based on early thermodynamic calculations, which possess significant limitations. Currently, there is a dearth of research data on the behavior of REEs in carbonate/phosphate systems, and the theoretical framework remains incomplete. Therefore, conducting thermodynamic investigations into REEs in carbonatites holds immense significance and practical value. The range of existence for REE–OH complexes is constrained due to insufficient thermodynamic data and limited research efforts that have only focused on a few elements, resulting in a scarcity of available reliable information.

In addition, further comprehensive investigations are still required, including into the significantly higher degree of fluorination observed in Y compared to other REEs [177] and the general absence of Sc combining with common mineralization anions. These distinctive elemental properties necessitate additional supplementation; moreover, there exists a wide range of organic ligands whose physicochemical characteristics undergo alterations under both high and low temperatures. Therefore, it is imperative to conduct extensive research on REE organic complexes.

8. Conclusions

Based on the geological observations on REE mobility and mineralization, as well as the published data on REE solubility, speciation in hydrothermal solutions, and related thermodynamic calculations, this paper reviewed and compared the complexation and REE transport capacity of various hydrothermal fluids. The major conclusions are as follows:

- (1) Zero or weak hydrolysis of REE ions suggests that the predominant forms of REEs in solution are REE ions or hydrated ions in low-temperature and acidic–weakly basic fluids.
- (2) Cl^- , SO_4^{2-} , and OH^- are the main ligands for transporting REEs, while F^- , CO_3^{2-} , and PO_4^{3-} are the ligands for depositing REEs. Organic matter may also be a complexing ligand for the transport of REEs.
- (3) The REE transport abilities of different ligands with similar concentrations under high-temperature ($T > 300\text{ }^\circ\text{C}$) acidic or alkaline conditions follow the order: $\text{Cl}^- \approx \text{SO}_4^{2-} > \text{F}^- \approx \text{PO}_4^{3-} > \text{CO}_3^{2-} > \text{OH}^-$ (acidic conditions); $\text{OH}^- > \text{SO}_4^{2-} \approx \text{Cl}^- > \text{F}^-$ (alkaline conditions). REE- CO_3^{2-} -OH complexes may exhibit greater transport abilities for REEs under alkaline conditions.
- (4) The transport of REEs is affected by the ligand types and environmental factors such as temperature, pressure, pH, and the ligand activity in fluids. A scenario with high temperature, low pH, high ligand content, and high salinity will enhance the dissolution and transport of REEs in hydrothermal fluids.

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