Earth Planet. Sci. Lett. 647 (2024) 119046

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Rhenium isotope variations in Icelandic groundwaters and hydrothermal systems

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ARTICLE INFO

Editor: Dr. F. Moynier

Keywords:
Rhenium
Rhenium isotopes
Groundwater
Hydrothermal
Paleo proxy
Oceanic mass balance

ABSTRACT

The isotopic composition of rhenium (Re) has potential for use as a proxy to infer changes in seafloor redox and/or global oxidative weathering intensity. Despite an emerging dataset on this nascent isotope system in Earth's surficial environments, very little is known about processes that control Re isotope fractionation, nor the isotopic composition of hydrothermal systems. Here we present Re concentrations and Re isotopic compositions (reported as δ^{187}Re, relative to NIST 3143) of groundwaters and hydrothermal fluids from three Icelandic settings. First, we show that high-temperature fluids that have experienced vapour-phase segregation (boiling) from the Reykjanes peninsula and the Hengill volcanic system have the highest δ^{187}Re values (−0.01 to +0.34 ‰) observed to date, inferred to result from Re isotope fractionation during incorporation of Re into secondary reduced minerals. Second, we examine the Mývatn area in northern Iceland, which has both cold and warm groundwaters. Cold groundwaters (< 10 °C) have δ^{187}Re values indistinguishable from Icelandic basalts (−0.36 to −0.32 ‰) whilst warm waters have higher δ^{187}Re (−0.31 to +0.19 ‰) which increase with increasing temperature (up to 45 °C). The variation of δ^{187}Re in Mývatn groundwaters is closely mirrored by variations in δ^{98}Mo, consistent with mixing between compositionally distinct water end-members. Finally, geothermal waters from the Geysir field have variable Re concentrations and δ^{187}Re values (−0.23 to +0.34 ‰), likely reflecting multiple physico-chemical processes. Using these results, we show that hydrothermal activity is unlikely to exert a large net impact on the seawater Re budget, nor the secular changes in seawater δ^{187}Re. These findings also point toward developing a novel Re isotope tracer for redox processes.

1. Introduction

Rhenium (Re) isotopes have emerged as a promising tool to track and reconstruct processes operating in Earth's critical zone of rock weathering (Miller, 2009; Miller et al., 2015; Dickson et al., 2020; Dellinger et al., 2021). Rhenium is a transition metal, present conservatively in the open ocean with typical concentrations of ~7.4 pg/g (Anbar et al., 1992; Colodner et al., 1993; Dickson et al., 2020) and has a long seawater residence time of ~1.3 × 10^5 years (Miller et al., 2011). As a redox-sensitive element, Re is known for valence states between 1− and 7+. In oxygenated waters (Eh > 0 volts) and over a wide range of pH values (~5.5 to 9.5), the highly soluble perrhenate oxyanion (ReO_4^-) is the dominant species of Re (Nikolaychuk, 2022). Under reducing conditions, Re(VII) may be reduced to less soluble Re(IV) that is in the form of ReO_2 and/or ReS_2 (Yamashita et al., 2007; Chappaz et al., 2008), or be complexed with dissolved sulfide to form thioperrhenate ($ReO_xS_{4\text{-}x}{}^-$)

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https://doi.org/10.1016/j.epsl.2024.119046
Received 16 April 2024; Received in revised form 22 September 2024; Accepted 26 September 2024

or Re(VII)-sulfide precipitates (Helz and Dolor, 2012; Vorlicek et al., 2015). Removal of Re may also occur via co-precipitation at surfaces of a Fe–Mo–S colloidal phase in sulfidic waters (Helz and Dolor, 2012; Helz, 2022). As Re is extraordinarily enriched in suboxic and anoxic marine sediments (mean concentration 65.5 ng/g, e.g., Dubin and Peucker-Ehrenbrink, 2015; Sheen et al., 2018) relative to its low crustal value (~0.2 to 2 ng/g, e.g., Peucker-Ehrenbrink and Jahn, 2001; Sun et al., 2003), its elemental abundance, combined with other redox-sensitive trace metals, can be an effective proxy for tracking O_2-deficient conditions (Bennett and Canfield, 2020; Calvert and Pedersen, 2007; Živković et al., 2023).

To use the Re system to track redox processes, we require thorough knowledge of the surface Re mass budget. Rivers are the main source of dissolved Re to the oceans in the present-day (Miller et al., 2011; Sheen et al., 2018), with a global discharge-weighted (pre-anthropogenic) concentration of ~2 pg/g, which accounts for an input flux of $\sim 4.3 \times 10^5$ mol/yr (Miller et al., 2011; Dellinger et al., 2021). In sedimentary rocks, a proportion of Re may be organically bound (Cohen et al., 1999; Rooney et al., 2012). Oxidative weathering releases CO_2 from these rocks, while oxidised Re is released to river waters as soluble ReO_4^-; riverine dissolved Re fluxes strongly link to modern-day weathering rates (Dalai et al., 2002; Jaffe et al., 2002; Hilton et al., 2014; Zondervan et al., 2023). Although groundwaters are usually assumed subordinate to the global riverine discharge, they may play an overlooked role in contributing to the oceanic mass balance of metals and their isotopes (e.g., Neely et al., 2018; Mayfield et al., 2021). In addition, the role of hydrothermal activity in the geochemical cycling of redox-sensitive elements has garnered increased attention (e.g., Morford and Emerson, 1999). Rhenium may be stabilised by forming chloride complexes in hydrothermal solutions (Xiong and Wood, 2002), or it may be precipitated with sulfides, leaving very low dissolved Re concentrations (~1 to 10 pg/g) in residual fluids (Xiong and Wood, 2001). Measurements on hydrothermal fluids/sediments suggest seafloor hydrothermal circulation through the oceanic crust likely represents a sink of Re in the oceans (Miller et al., 2011; Colodner et al., 1993).

Rhenium has two isotopes, ^{187}Re and ^{185}Re, which comprise ~63 % and 37 % of natural Re respectively. The ^{187}Re isotope is radioactive, but decays with a very long half-life (4.12×10^{10}yr; Smoliar et al., 1996), making the isotope ratio of ^{187}Re and ^{185}Re more analogous to a stable isotope system. Theoretical calculations suggest that changes in the chemical speciation and oxidation state of Re can induce isotopic fractionation of up to ~1.5 ‰ (Miller et al., 2015), with the ReO_4^- oxyanion predicted to be enriched in ^{187}Re compared to thiolated Re(VII)-S and reduced Re(IV) species. New analytical and sampling method developments (Dellinger et al., 2020) have resulted in a small, but growing dataset of δ^{187}Re measurements to evaluate the Re cycle. The δ^{187}Re value (relative to NIST 3143) of Atlantic seawater is determined to be -0.17 ± 0.12 ‰ (2SD, $n = 12$; Dickson et al., 2020), higher than that of igneous rocks (−0.45 to −0.22 ‰; Wang et al., 2024). The δ^{187}Re values for dissolved Re in Mackenzie River waters (-0.29 ± 0.09 ‰, 2SD, $n = 10$; Dellinger et al., 2021) coincide with a proposed 'terrestrial baseline' value (-0.33 ± 0.15 ‰, 2SD, $n = 14$; Wang et al., 2024), while corresponding river sediments show offsets to lower values (−0.52 to −0.27 ‰; Dellinger et al., 2021), possibly due to preferential oxidation of reactive phases with heavy δ^{187}Re. Sedimentary rock from the New Albany shales also exhibit very low δ^{187}Re values (~ −0.6 ‰; Miller et al., 2015). These available Re isotope data hint at notable isotopic variability during the surface cycling of Re, both in terms of weathering on land, and in terms of isotopically light oceanic Re sinks and/or input of Re to the oceans from other sources that are yet to be discovered (Dickson et al., 2020).

This study aims to quantify the behaviour of Re isotopes in high- and low-temperature hydrothermal fluids and groundwaters, and to test whether these fluids have the potential to impact on the oceanic isotope mass balance of Re as an isotopically distinct input flux. Water samples were collected in September 2021 from (1) the Mývatn groundwater system in northeast Iceland, (2) four high-temperature geothermal sites located on the Reykjanes peninsula and the Hengill volcanic system of southwest Iceland, and (3) the Geysir field in the southern lowlands of Iceland (Fig. 1). We report dissolved Re concentrations and Re isotopic compositions, together with ancillary data (major and trace element concentrations). The implications of these results for the geochemical cycling of Re in the modern day and in the geological past are discussed.

2. Geological setting

Iceland is located along the Mid-Atlantic Ridge, where the North American and European plates diverge. The anomalously high magma productivity that created Iceland as the subaerial expression of the ridge is commonly attributed to a thermal mantle plume. The divergent plate boundary produces dominantly basaltic lavas (>80 %) and widespread hydrothermal activity associated with both active volcanic centres, where the high-temperature systems are mainly hosted, and off-axis fractures (e.g., Fridleifsson, 1979) (Fig. 1).

Lake Mývatn is a shallow eutrophic lake in NE Iceland, almost entirely groundwater fed, with cold and warm springs feeding the southern and the northern basins, respectively. Groundwaters in the Mývatn region are possibly influenced, to variable degrees, by the adjacent Krafla and/or the Námafjall geothermal fields (Kristmannsdóttir and Ármannsson, 2004; Ólafsson et al., 2015), and are conventionally divided into six distinct groups based on stable water isotope (δ^2H and δ^{18}O) values (Ármannsson et al., 2000; Óskarsson, 2019). These waters may also be influenced by atmospheric deposition (e.g., Nelson et al., 2022; see Suppl Info Text S1 for details). The Mývatn region that is dominated by basalts has been routinely monitored by the Icelandic GeoSurvey (ÍSOR) (Neely et al., 2018; Óskarsson et al., 2021); samples from this study were collected from ten sites spanning 'cold' groundwaters (< 10 °C) to 'warm' springs/groundwaters (up to ~45 °C).

Several high-temperature geothermal systems occur in SW Iceland, of which Reykjanes, Svartsengi, Hellisheidi, and Nesjavellir were sampled (Fig. 1). At these sites, reservoir fluids that experience boiling during decompression (~240 to 320 °C) are discharged through geothermal wells (Ármannsson, 2016; Fowler et al., 2019). Fluids at Reykjanes are composed of seawater chemically modified by boiling and reaction with the basaltic host rock (Arnórsson, 1978), while at Svartsengi, they are a ~2:1 mixture of seawater and meteoric water that is modified by reacting with basalt (Ragnarsdóttir et al., 1984). Dilute fluids at Hellisheidi and Nesjavellir, which are associated with the Hengill volcanic system, are meteoric-sourced and are modified by the influx of magmatic gases and reactions with the host basalt (Ármannsson, 2016). At these four systems, secondary minerals form in the fluid reservoir at pressures between 0.8 and 2.8 MPa (Fowler et al., 2019).

The Geysir area is hosted by basaltic lavas and more evolved rhyolitic dome lavas. The main geothermal activity is associated with boiling hot springs, alongside acid pools and small mudpots found within the main spring area (Arnórsson, 1985). In this study, boiled alkaline water, steam-heated acid water, and mixed geothermal water were collected (Figure S1). Previous studies have documented highly variable temperatures (20–100 °C), pH (2.5–9.8) and total dissolved solids (~100–1000 μg/g) in these distinct types of waters (Kaasalainen and Stefánsson, 2012; Kaasalainen et al., 2017).

3. Methods

3.1. Sample collection and pre-concentration

The cold and warm groundwaters at Mývatn were collected during routine sampling carried out by ÍSOR (Óskarsson et al., 2021). High-temperature reservoir fluids at the Reykjanes peninsula were sampled with the help of HS Orka and Reykjavík Energy at the wellheads using a Webré vapor-water separator according to established methods

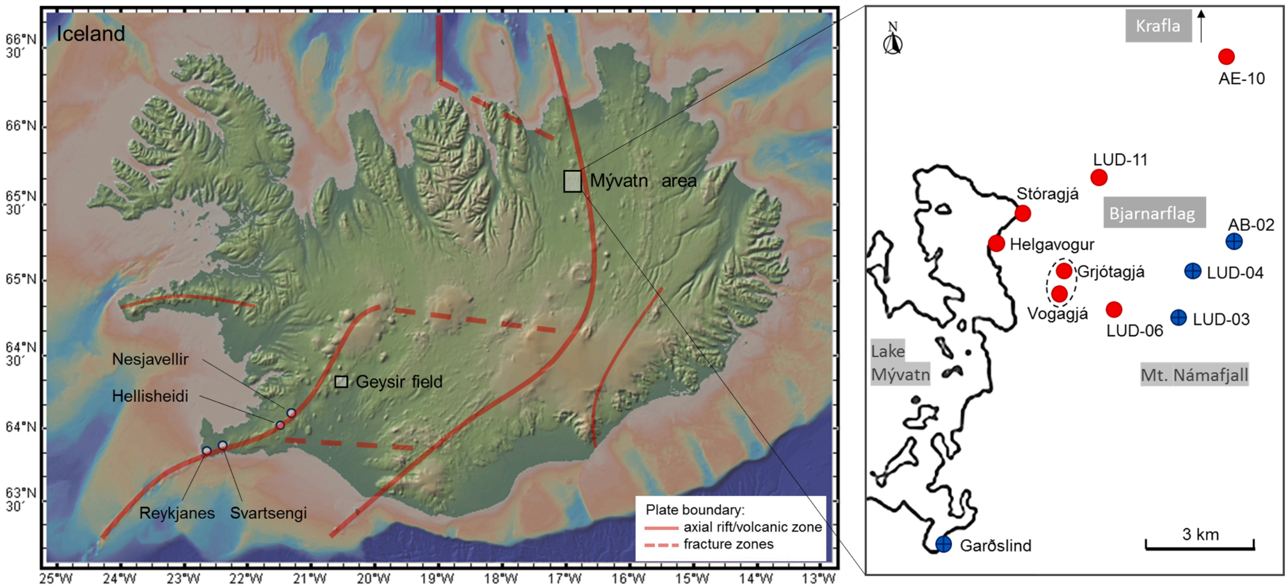

Fig. 1. Sampling locations in Iceland: Mývatn area, Geysir field, the Reykjanes, Svartsengi sites (on the Reykjanes peninsula) and Hellisheidi/Nesjavellir sites (associated with the Hengill volcanic system). Map courtesy of http://www.geomapapp.org. Sampling sites in the Mývatn area are also shown, wherein blue symbols represent 'cold' groundwater and red for 'warm' spring/groundwaters; the 'Group V' sites (Grjótagjá and Vogagjá) that are influenced by fluids/effluents from the Bjarnarflag geothermal field, rather than Krafla (Neely et al., 2018; Óskarsson, 2019) are marked.

(Arnórsson et al., 2006). The sampling at Geysir field was guided by Umhverfisstofnun, The Environment Agency of Iceland. Water samples of ~10 L for Re isotope analysis were initially collected into acid-cleaned LDPE cubitainers (Cole-Parmer®) prior to Re pre-concentration using the methods of Dellinger et al. (2020).

Immediately following water sampling, these samples were filtered through an AcroPak 200 (Supor™, Pall corporation) filter capsule (0.2 μm, with 0.8 μm pre-filter), acidified with thermally distilled HCl to pH~2, and transferred into 20 L sterile double-lined PE bags. The sample was weighed and the bag was connected with a custom fitting to a BioRad Econo-Pac® 20 mL column that was filled with ~4 mL of pre-cleaned AG1-X8 resin (Dellinger et al., 2020, 2021). In a field 'laboratory', filtered water samples were passed through the column by gravity flow. The Re-loaded columns were then capped and double bagged. In the clean laboratory, 50 mL of 1 M HCl was passed through the column to remove some matrix elements. The Re fraction was then eluted with 30 to 40 mL of 7.5 M HNO_3 and was collected in an acid cleaned PFA vial (Savillex). Finally, the sample was evaporated to dryness and reconstituted in 1 M HCl.

3.2. Dissolved Re and Re isotope analysis

The Re concentrations of the samples were determined by an isotope dilution method. Approximately 50 mL aliquot (filtered) was weighed into clean PFA vials and a known amount of ^{185}Re single spike was added to each sample. Following equilibration, the sample was evaporated to dryness and subsequently taken up in 2 M HNO_3. Rhenium was then extracted using 3-methyl-1-butanol (isoamylol) (Birck et al., 1997). The purified samples were re-dissolved in 3 % HNO_3 and were measured using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS; Neptune Plus) at Royal Holloway University of London. The Re concentration was derived based on the ^{185}Re/^{187}Re ratio of the sample/spike mixture.

For the determination of isotopic composition, Re was separated from sample matrix via a three-step column procedure described in Dellinger et al. (2020) and Dickson et al. (2020). First, 2 ml AG1-X8 (200–400 mesh) anion exchange resin was loaded into polypropylene BioRad columns and was cleaned and pre-conditioned. Samples were loaded onto the columns in 1 M HCl, with further additions of 1 M HCl and 3 M HNO_3 to remove matrix elements and transition metals. The Re purification was repeated two more times using 200 μL AG1-X8 resin in Teflon micro-columns. After each column step, Re was eluted with 7.5 M HNO_3 and samples were refluxed in concentrated HNO_3 at 120 °C for at least 24 h to destroy resin-derived organic residues.

The Re isotopic composition of the samples was determined by MC-ICP-MS (Neptune Plus) at Royal Holloway University of London, using methods described in Dickson et al. (2020). Briefly, purified samples were introduced in wet plasma mode using a quartz stable introduction system (SIS) spray chamber. Instrumental mass bias was corrected by doping each sample to 30 ppb W with NIST SRM 3163, and by using an exponential law with the measured ^{186}W/^{184}W (Miller et al., 2009). To allow precise measurement at concentrations of ~5 ppb (sample solution of $>$ 1 mL), ^{185}Re and ^{187}Re signals were monitored with Faraday detectors equipped with 10^{13} Ω amplifiers. Each analytical sequence consisted of repeat analyses of the NIST3143 and NIST989 standard reference materials (SRM) with every three samples. The final Re isotopic composition of the samples is reported in delta notation relative to NIST SRM 3143 and expressed as:

$$\delta^{187}\mathrm{Re}(‰) = \left[\left(^{187}\mathrm{Re}/^{185}\mathrm{Re}\right)_{\mathrm{sample}} \Big/ \left(^{187}\mathrm{Re}/^{185}\mathrm{Re}\right)_{\mathrm{NIST3143}} - 1\right] \times 1000 \quad (1)$$

All Re data are given in Table 1. Procedural blanks were below 10 picograms, which was $<$ 1 % of the total Re analysed. The recovery of Re was $>$ 75 % for all samples, which does not induce measurable Re isotopic fractionation (Miller et al., 2009; Dellinger et al., 2020). The precision and accuracy of the above methods were further validated through the analysis of (1) NIST 989 and ICP Re standard solutions, and (2) inter-comparison samples, including USGS reference materials BIR-1 and BCR-2, alongside Bermuda Atlantic Time-Series (BATS) seawater (Table S1).

3.3. Ancillary analyses

Hydrogen sulfide (H_2S) was detected immediately upon collection of water samples, by titrating with mercuric acetate in alkaline solution with dithizone in acetone as colour indicator. Total dissolved solids (TDS) were determined based on the total mass of dissolved minerals

Table 1

Rhenium data for all water samples measured in this study, together with ancillary data.

Station	Sample ID	Description	Latitude °N	Longitude °W	Temp [a] (°C)	pH	δ^{187}Re (‰) *1st measurement*	2SE [b]	δ^{187}Re (‰) *2nd measurement*	2SE	**δ^{187}Re (‰)** *Average*	2SD [c]	**Re (pg/g)**	H_2S (μg/g)	SO_4^{2-} (μg/g)	Na (μg/g)	Mo (ng/g)
Mývatn																	
AB-02	M02	cold groundwater	65.632	−16.774	4	7.9	−0.32	0.06	−0.40	0.08	**−0.36**	0.10	**1.28**	<0.03	11.5	9.4	0.30
LUD-04	M03		65.625	−16.803	5	8.0	−0.33	0.08	−0.31	0.09	**−0.32**	0.10	**1.23**	<0.03	63.2	36.2	0.93
LUD-03	M05		65.612	−16.813	6	8.3	−0.30	0.07	−0.41	0.07	**−0.35**	0.15	**2.21**	<0.03	13.8	16.5	0.60
Garðslind	M07		65.553	−16.969	6	8.7	−0.36	0.07	−0.31	0.07	**−0.33**	0.10	**2.00**	<0.03	7.4	18.4	0.71
Helgavogur	M09	warm spring/groundwater	65.634	−16.923	23	8.3	−0.31	0.08			**−0.31**	0.10	**2.60**	<0.03	62.0	51.1	0.86
Grjótagjá	M14		65.626	−16.883	45	8.3	0.02	0.06	0.13	0.14	**0.07**	0.15	**0.40**	0.03	85.0	78.4	0.20
Stóragjá	M15		65.638	−16.910	27	8.3	−0.24	0.07	−0.22	0.09	**−0.23**	0.10	**2.26**	<0.03	77.5	59.5	0.94
Vogagjá	M16		65.619	−16.889	40	8.4	−0.08	0.07	−0.13	0.06	**−0.10**	0.10	**0.52**	<0.03	108.4	81.7	0.22
AE-10	M18		65.681	−16.775	36	8.1	0.19	0.06	0.20	0.12	**0.19**	0.12	**0.50**	<0.03	70.1	42.2	0.59
LUD-06	M20		65.615	−16.853	33	8.2	−0.23	0.08	−0.14	0.09	**−0.18**	0.12	**1.42**	<0.03	57.1	49.5	0.79
LUD-11	M21		65.649	−16.862	32	7.7	−0.19	0.06	−0.20	0.06	**−0.19**	0.10	**2.56**	<0.03	91.0	60.8	0.84
SW Iceland																	
Reykjanes	RN12	high-temperature reservoir fluid	63.825	−22.679	*26*	6.7	0.03	0.07	−0.04	0.07	**−0.01**	0.10	**7.06**		8.4		
Reykjanes	RN24		63.825	−22.679	*24*	6.7	0.30	0.08	0.38	0.12	**0.34**	0.12	**3.16**		7.9		
Svartsengi	SV7		63.877	−22.433	*22*	6.8	0.32	0.10	0.31	0.16	**0.31**	0.16	**1.28**		16.8		
Hellisheidi	HE5		64.049	−21.373	*32*	8.2	0.28	0.07	0.34	0.08	**0.31**	0.10	**2.12**				
Nesjavellir	NG7		64.106	−21.255	*33*	8.1	0.07	0.08			**0.07**	0.10	**0.65**				
Nesjavellir	NG10		64.100	−21.256	*29*	8.3	0.13	0.09	0.09	0.07	**0.11**	0.10	**0.61**				
Geysir field																	
Ótherrishola (GY1) boiled water			64.312	−20.302	*31*	7.4	−0.23	0.09			**−0.23**	0.10	**6.47**		90.8		
N. of Geysir (GY2) mixed water			64.314	−20.300	21	6.7	0.34	0.07			**0.34**	0.10	**2.98**		98.3		
N. of Geysir (GY3) acidic water			64.315	−20.299	21	2.7	−0.23	0.10			**−0.23**	0.10	**1.01**		147.5		

[a] Temperature measurements for high-temperature fluids collected from SW Iceland and one boiled alkaline water from Geysir (shown in *italic*) were done on sample aliquots as soon as they were collected, but cooling has occurred; the pH of these samples also refers to the pH at the measured temperature. Temperature measurements at all other sites reflect real in-situ condition.

[b] 2SE is the internal error of each individual MC-ICP-MS measurement.

[c] Uncertainties (2SD) on δ^{187}Re represent 2 standard deviation of repeat MC-ICP-MS measurements on the same sample (or 2SE internal error if there was only one measurement), or the long-term reproducibility for the standard solution (ICP: 0.10 ‰; Table S1), whichever is larger.

after drying the samples. Anions (sulfate, chloride, etc.) were measured on separate sample aliquots by ion chromatography using a suppressed conductivity detection method at Durham University (Gjerde et al., 1979). Additional metal concentrations were measured either with ICP-OES (e.g., for silicate, sodium, potassium, magnesium, boron) at the ÍSOR laboratory or with ICP-MS (e.g., for molybdenum, vanadium and iron) at the ALS laboratory in Sweden. All H_2S, TDS and metal concentration data have been previously reported in Óskarsson et al. (2021). These ancillary data are also shown in Table 1 and Table S2.

4. Results

4.1. Rhenium and sulfate concentrations

Dissolved Re concentrations for water samples in this study ranged from 0.40 to 7.06 pg/g. Sulfate (SO_4^{2-}) concentrations ranged between 7.4 and 147.5 μg/g. Our measured Re and SO_4^{2-} concentrations are comparable to those reported for global river waters (Miller et al., 2011; Rahaman et al., 2012; Hilton et al., 2014; Horan et al., 2017; Fig. 2), but there is no systematic relationship between Re and SO_4^{2-}.

Cold groundwaters draining the Mývatn basaltic terrain had a mean Re concentration of 1.68 ± 1.00 pg/g (2SD, $n = 4$), lower than previously reported for groundwaters where the drainage lithologies contain carbonate rocks or black shales (1.3–26 pg/g: Hodge et al., 1996; Colodner et al., 1993). At Mývatn, whilst no clear relationship was observed between Re and temperature or the relatively mobile components that were measured (Figure S2a), the lowest Re concentrations (0.40 to 0.52 pg/g) were found in the highest temperature spring/groundwaters (36–45 °C) (Table 1).

The highest Re concentrations in this study were found in one high-temperature reservoir fluid (7.06 pg/g, from the Reykjanes site) and in a boiled alkaline water (6.47 pg/g, from the Geysir field) sample; these concentrations are close to seawater values (~7.2 to 7.6 pg/g). Note also that seawater-fed reservoir fluids (3.16 to 7.06 pg/g) from the Reykjanes peninsula had higher Re concentrations than meteoric-sourced dilute fluids (0.61 to 2.12 pg/g) from the Hengill volcanic system (Table 1).

Generally, high-temperature reservoir fluids, and most cold Mývatn groundwaters had lower SO_4^{2-} concentrations compared to other water samples collected from the Mývatn and the Geysir areas (Fig. 2; Figure S3a). Consistent with previous studies (e.g., Kaasalainen et al., 2017; Neely et al., 2018; Fowler et al., 2019), in situ pH of all samples collected was slightly alkaline or near neutral, except for one sample from the Geysir field (Figure S3a).

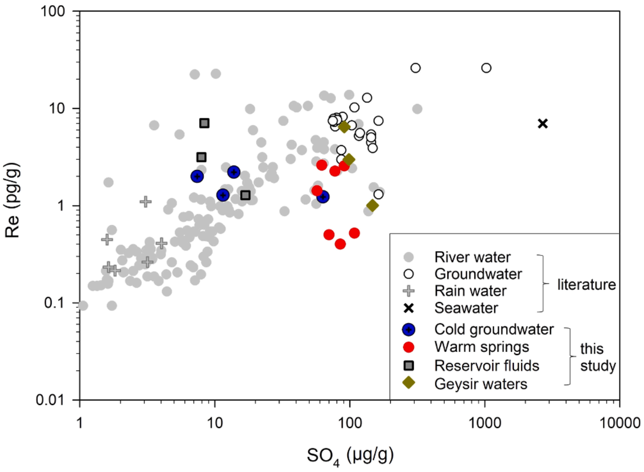

Fig. 2. Cross plot of dissolved Re versus sulfate concentrations, for new data from this study (cold groundwater and warm spring/groundwaters (●) from the Mývatn area, high-temperature reservoir fluids (■) from the Reykjanes peninsula, and geothermal waters (◆) from the Geysir field) together with river water, groundwater, rain water and seawater data from the literature (Hodge et al., 1996; Miller et al., 2011; Rahaman et al., 2012; Hilton et al., 2014; Horan et al., 2017; Dickson et al., 2020).

4.2. Rhenium isotopic composition

Rhenium in cold (< 10 °C) Mývatn groundwaters (δ^{187}Re = −0.36 to −0.32 ‰) was isotopically indistinguishable from Icelandic basalts (δ^{187}Re = −0.35 to −0.28 ‰; Wang et al., 2024), and appeared to be very slightly lighter than previously reported Mackenzie river waters (δ^{187}Re = −0.33 to −0.21 ‰; Dellinger et al., 2021) (Fig. 3). Warm spring/groundwaters (23–45 °C) at the Mývatn area exhibited a systematic increase in δ^{187}Re values (−0.31 to up to +0.19 ‰) with increasing temperature (Fig. 4a).

In high-temperature reservoir fluids collected from geothermal wells from the Reykjanes peninsula and Hengill volcanic system, δ^{187}Re values were notably higher (−0.01 to +0.34 ‰, mean δ^{187}Re = +0.19 ± 0.30 ‰, 2SD, $n = 6$; Table 1) than cold Mývatn groundwaters and Icelandic basalts. No statistically significant differences in δ^{187}Re were observed among different types of reservoirs, and these values represent the heaviest Re isotopic compositions of terrestrial materials observed to date. Three additional samples (boiled alkaline water, steam-heated acid water and mixed geothermal water) from the Geysir field also showed relatively high δ^{187}Re values (−0.23 to +0.34 ‰; Table 1).

4.3. Mývatn and Geysir environmental settings

At Mývatn, there was a general increase in the concentration of aqueous components TDS, SO_4^{2-}, SiO_2, Na and K with increasing water temperature (Figure S3b). Temperature can serve as an indicator of a hydrothermal contribution to this system: warm springs (> 10 °C) have been considered as hydrothermally influenced groundwaters (Neely et al., 2018). There appear to be kinks in the correlations between these

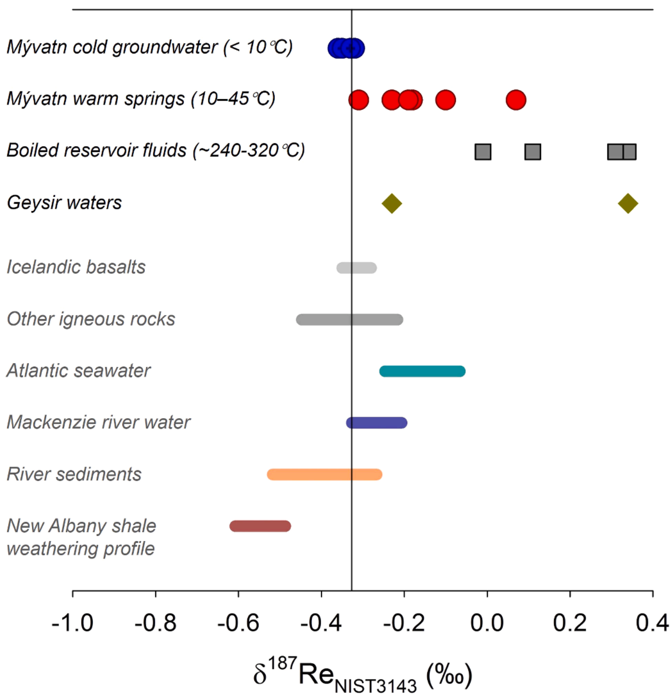

Fig. 3. Rhenium isotope data from this study and from the literature: Icelandic basalts (Wang et al., 2024); other igneous rocks (Wang et al., 2024); Atlantic seawater (Dickson et al., 2020); Mackenzie river water and river sediments (Dellinger et al., 2021); New Albany shale weathering profile (Miller et al., 2015). A proposed terrestrial baseline δ^{187}Re value (−0.33 ‰; Wang et al., 2024) is shown as vertical line.

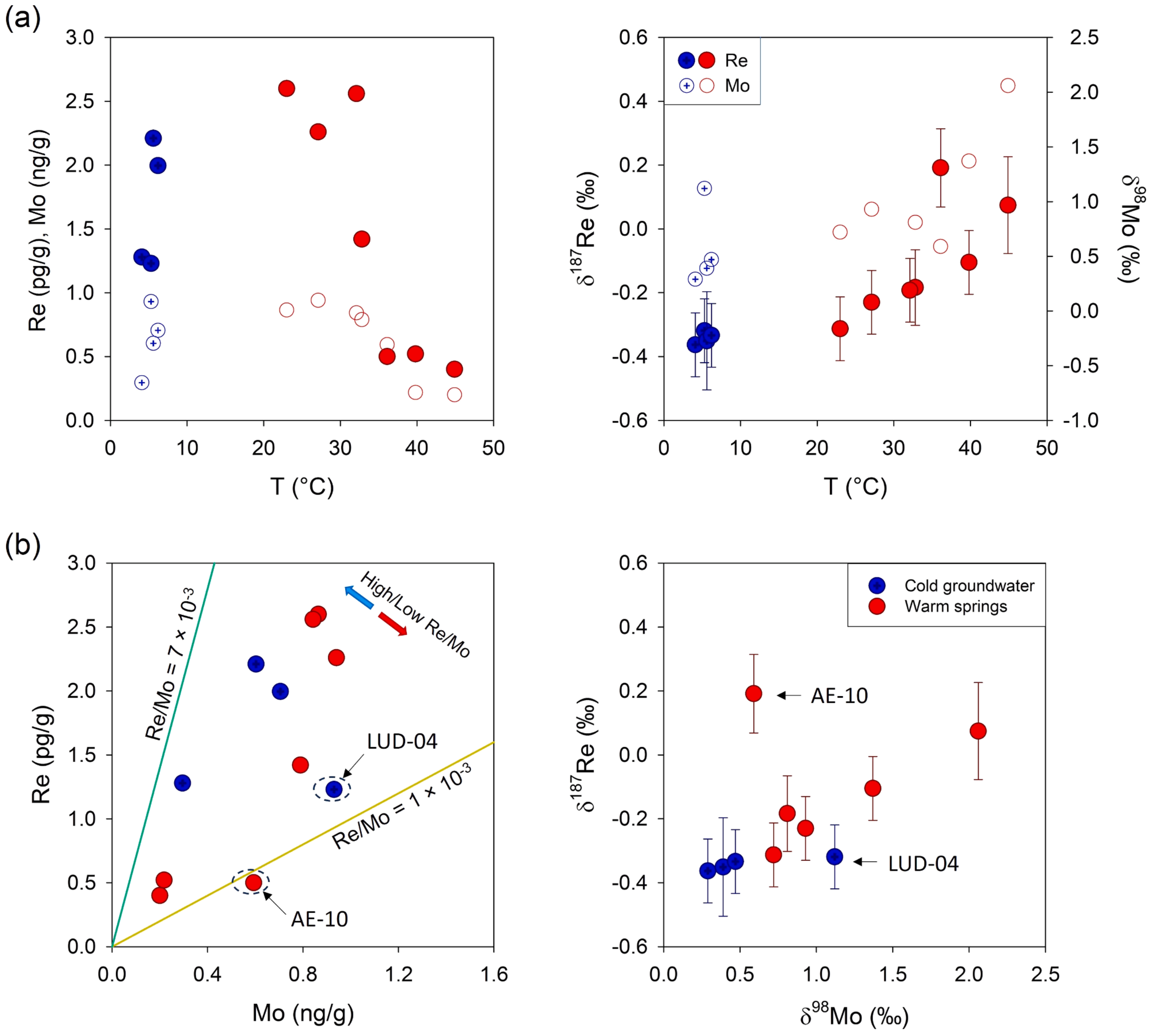

Fig. 4. **(a)** Changes in dissolved Re and Mo concentrations, and dissolved Re and Mo isotope values, as a function of temperature for water samples collected from the Mývatn area. Blue symbols represent cold groundwater and red for warm springs; filled circles are for Re and open circles for Mo. Mo concentrations are determined in this study (and they are comparable to those reported in Neely et al. (2018) except for samples LUD-04 and AE-10, which is discussed in Figure S4). δ^{98}Mo values are from Neely et al. (2018). Error bars on Re and Mo concentrations are smaller than the size of symbols. Error bars on δ^{187}Re are explained in Table 1. **(b)** The relationships between dissolved Re and Mo concentrations, and between dissolved Re and Mo isotope values, for water samples collected from the Mývatn area. The average seawater and Icelandic basalt Re/Mo mass ratios (respectively 7×10^{-3} and 1×10^{-3}) are shown as the straight lines. The samples LUD-04 and AE-10 are marked.

aqueous components and the temperature, wherein samples LUD-04 and AE-10 showed obvious offsets from the correlation (Figure S3b). Excluding these two samples, measured dissolved molybdenum (Mo) concentrations in this study are consistent with those reported in Neely et al. (2018) (samples were collected from the same sites but during different sampling campaigns; Figure S4). Note also that the so-called 'Group V' samples (Grjótagja and Vogagjá) exhibited the largest deviations from the meteoric water line (δ^2H−δ^{18}O; Figure S3c) and were thought to have a distinct source of hydrothermal input (Neely et al., 2018). The chloride (Cl) content of Mývatn water samples was correlated to boron (B) (Figure S3c), both of which are typical mobile elements during water-rock interaction. The Cl/B ratio (as derived from the slope of the correlation) was ~47, broadly consistent with their source from basaltic rock (~15 to 50; Arnórsson and Andrésdóttir, 1995).

The GY1 sample collected from Ótherrishola at the Geysir field represents alkaline water that has experienced boiling, which was thought to contain significant geothermal aquifer fluid component and be controlled by secondary mineral-fluid equilibria (Kaasalainen and Stefánsson, 2012). The GY2 sample taken from north of the Geysir main spring is supposed to represent a mixture of boiled alkaline water, steam-heated acid water, and non-thermal ground/surface waters (Kaasalainen and Stefánsson, 2012; Kaasalainen et al., 2017). The GY3 sample from north of Geysir is steam-heated acid water and had a pH of ~2.7 that is related to high levels of SO_4^{2-} (Kaasalainen and Stefánsson, 2012).

5. Discussion

5.1. Mixing processes that cause δ^{187}Re variations in Mývatn groundwaters

The δ^{187}Re value of Mývatn cold groundwaters was tightly constrained at −0.34 ± 0.04 ‰ (2SD, $n = 4$) (Figs. 3, 4a), which is identical to that of Icelandic basalts (−0.31 ± 0.06 ‰, 2SD, $n = 6$; Wang et al., 2024). This similarity suggests that there is no resolvable Re isotopic fractionation during dissolution of primary basaltic minerals. Rhenium in the Mývatn system is likely derived from chemical weathering of plagioclase, hydrated basaltic glass and olivine during water-rock interaction (Suppl Info Text S1); these minerals are predicted to be undersaturated in cold groundwater conditions (Neely et al., 2018), suggesting the potential to dissolve. By contrast, pyroxene and magnetite tend to remain oversaturated (Neely et al., 2018). There is currently no available δ^{187}Re data for mineral separates. However, minimal Re isotopic fractionation was determined on a suite of related lavas spanning a range of magmatic evolution at Hekla volcano, Iceland (Wang et al., 2024). Therefore, incongruent mineral dissolution is unlikely to shift the δ^{187}Re signature of the host basalt. Similarly, studies on Mo isotopes in groundwaters suggested negligible Mo isotopic fractionation at initial stages of chemical weathering (King and Pett-Ridge, 2018; Neely et al., 2018). Rhenium is often discussed together with Mo because of their shared geochemical behaviours as redox-sensitive elements (e.g., Miller et al., 2011). Note, however, that Mo can be less mobile relative to Re at later stages of weathering as (i) Mo and Re may not be hosted by the same mineral phase (e.g., Zhao et al., 2023) and (ii) Mo can be removed from solution during secondary mineral formation and/or via adsorption by organic matter which can induce an isotope effect (e.g., Dahl et al., 2017; Horan et al., 2020).

At Mývatn, δ^{187}Re values increased with increasing water temperature (notably at > 20 °C; Fig. 4a). The Mo isotope values (δ^{98}Mo) for water samples collected from this area (reported in Neely et al., 2018) showed similar trends towards higher values with increasing temperature (Fig. 4a). If we exclude the two samples LUD-04 and AE-10 that do not show consistent Mo concentrations with the literature (Section 4.3; Figure S4), there is a positive correlation ($p < 0.05$) between δ^{187}Re (this study) and δ^{98}Mo (Neely et al., 2018) for samples collected from the same sites within the Mývatn area (Fig. 4b). The correlation suggests that the main process suggested to control Mo isotope variation in this system, i.e. mixing between cold groundwater and hydrothermal end-members (Neely et al., 2018), may also be responsible for the Re isotope variation. Indeed, when δ^{187}Re is plotted against Na/Re or Mo/Re mass ratios, two distinct hydrothermal end-members are apparent (Fig. 5). Both the end-member (reservoir) fluids are characterized by heavier Re (and Mo) isotopic compositions relative to cold groundwaters (see further discussions in Section 5.2). However, whilst some of the warm spring/groundwater samples have slightly higher Re (and Mo) concentrations than cold groundwaters, indicating a hydrothermal input that is enriched in Re (and Mo), other samples (Grjótagja, Vogagjá and AE-10) have very low Re concentrations (0.40–0.52 pg/g) (Table 1; Fig. 6a). The samples Grjótagja and Vogagjá belong to ‘Group V’ that is thought to be influenced by fluids/effluents from the Bjarnarflag (Óskarsson, 2019), rather than the Krafla geothermal field; the latter is the main source for all other warm Mývatn waters. This additional geothermal source from Bjarnarflag is likely depleted in magnesium (Mg), vanadium (V) and Mo as well, indicated by the overall positive relationships between Re and these elements (Figure S2b). The depletion in Mo has been interpreted to be due to precipitation as sulfides (Neely et al., 2018).

Despite the striking δ^{187}Re-δ^{98}Mo relationship, the co-variation between dissolved concentrations of Re and Mo in this system is rather weak. The Re to Mo mass ratios in the Mývatn water samples range between ~ 0.8–4.3 × 10^{-3}. These values broadly coincide with Icelandic basalt (~1 × 10^{-3}; Wang et al., 2024) and seawater (~7 × 10^{-3}; e.g., Helz, 2022) ratios (Fig. 4b). Excluding sample LUD-04 that does not represent pristine groundwaters (there is likely hydrothermal input even though the water is cold: Óskarsson, 2019), the Re/Mo ratios in cold groundwaters (mean = 3.6 ± 1.5 × 10^{-3}, 2SD, $n = 3$) are generally higher than those in warm spring/groundwaters (2.2 ± 1.5 × 10^{-3}, 2SD, $n = 7$). This difference can be attributed to (i) a higher mobility of Re than Mo in cold groundwaters, as Mo can be lost due to secondary mineral formation as well as adsorption (Dahl et al., 2017; Horan et al., 2020), and (ii) a possibly lower Re/Mo ratio in both the hydrothermal end-members, which is analogous to high-temperature fluid samples collected from seafloor hydrothermal vents (Re/Mo < 1 × 10^{-3}: Miller et al., 2011). As will be discussed in Section 5.2, there are several processes that can result in loss of Re from the reservoir fluids such as degassing and incorporation into sulfide minerals.

It is also plausible that preferential loss of Re over Mo has occurred during mixing of groundwater and hydrothermal end-members. It is known that Re can become insoluble at less negative redox potentials than Mo such that Re may be sequestered at a shallower depth in

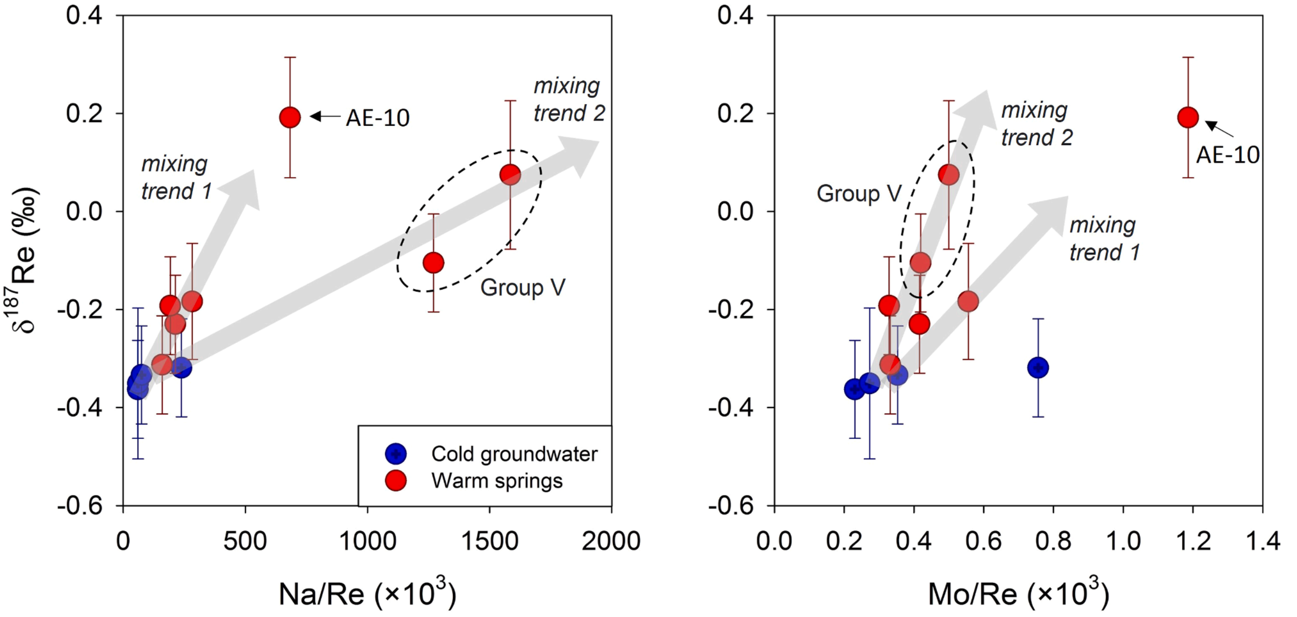

Fig. 5. Dissolved δ^{187}Re value plotted against Na/Re or Mo/Re mass ratios for all water samples collected from the Mývatn area. Both the δ^{187}Re–Na/Re and δ^{187}Re–Mo/Re relationships indicate that there are possibly two distinct hydrothermal end-members that can account for the Re isotope variations in the warm Mývatn spring/groundwaters (Section 5.1).

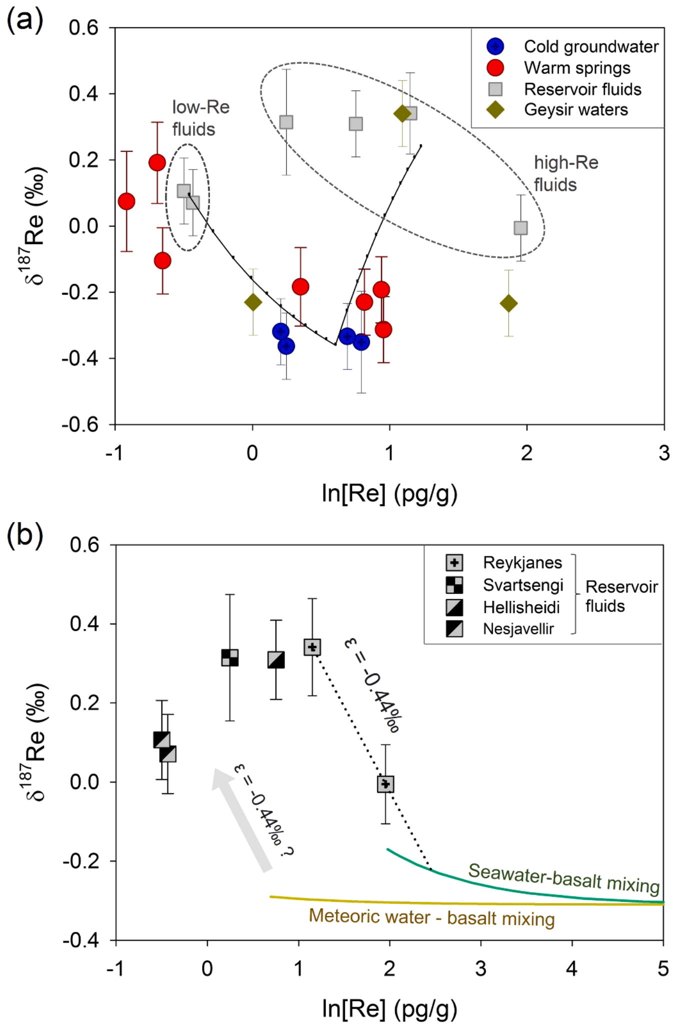

Fig. 6. Dissolved δ^{187}Re as a function of natural logarithmic Re concentration for **(a)** all water samples presented in this study, and **(b)** high-temperature reservoir fluid samples (note change in axis scales). In **(a)**, the two curves show the theoretical mixing trends between cold groundwater and high-temperature reservoir fluids: the reservoir fluids can be grouped into two, both are characterised by heavy δ^{187}Re but one is relatively enriched in Re (here represented by the Reykjanes, Svartsengi, and Hellisheidi fluids) and one is depleted in Re (represented by the Nesjavellir fluids) compared to pristine groundwater. Note that the composition of the Krafla/Bjarnarflag reservoir fluids (at Mývatn) will probably differ from the fluids collected from SW Iceland, so the mixing trends shown here do not necessarily fit the variations of δ^{187}Re–Re in Mývatn warm springs but can be used to support that there can be more than one hydrothermal end-member. In **(b)**, theoretical mixing curves of seawater–basalt and meteoric water–basalt are shown (Section 5.2). The dotted line indicates a possible Rayleigh-type fractionation that may be one explanation for the Re and δ^{187}Re variations at the Reykjanes sites, with an estimated Re isotope fractionation factor of ~ −0.44 ± 0.19 ‰ (error propagated based on the uncertainties of δ^{187}Re).

reducing sediments (e.g., Crusius et al., 1996). However, Re in nearly all of the Mývatn groundwaters are predicted to be in the oxidised form of ReO_4^- (based on Eh–pH; Figure S5) and the removal of Re by reduction is therefore not expected to occur. One exception may be AE-10, which represented the most reducing condition among all Mývatn sites according to Neely et al. (2018). The AE-10 sample did not have identical Mo concentration to Neely et al. (2018) (Figure S4), uncertainties remain in its 'real' Eh value at the time of our sampling. Since this sample has the lowest Re/Mo ratio (0.8×10^{-3}) and the highest δ^{187}Re value (+0.19 ‰) in the Mývatn system, the possibility that removal of a ^{185}Re-enriched phase from the fluid cannot be excluded. Note that AE-10 also exhibited very low sulfur isotope and strontium isotope ratios compared to all other Mývatn samples (Óskarsson, 2019), which may indicate processes of oxidation of H_2S and/or another hydrothermal source. On the other hand, the Mývatn springs may be formed, in part, as a consequence of steam heating (Neely et al., 2018; Óskarsson, 2019). Given the volatile behaviour of Re (e.g., Bernard et al., 1990), loss of steam may disproportionally deplete the springs in Re versus Mo. These additional processes during mixing may cause Re isotope fractionation. However, the degree of Re removal is likely not substantial in the majority of the warm Mývatn spring/groundwaters, so Re isotope variation may be masked by the mixing trends between the cold groundwater and the hydrothermal end-members that are, respectively, enriched in ^{185}Re and ^{187}Re (Fig. 5).

5.2. *Controls on δ^{187}Re in high-temperature reservoir fluids and Geysir geothermal waters*

Rhenium in high-temperature fluids from the basalt-hosted Reykjanes, Svartsengi, Hellisheidi and Nesjavellir sites is isotopically heavier (δ^{187}Re = −0.01 to +0.34 ‰) than Re in Mývatn cold groundwaters and Icelandic basalts. The direction of fractionation holds regardless of the type of fluid reservoir (seawater-fed versus meteoric-sourced). As discussed above, incongruent dissolution of basalt is not likely to induce a resolvable isotope effect for Re. Therefore, the δ^{187}Re variation in the high-temperature fluids can be first assessed by modelling simple conservative mixing processes involving seawater (δ^{187}Re = −0.17 ‰, Re = 7.41 pg/g: Dickson et al., 2020; Anbar et al., 1992) or meteoric water (δ^{187}Re = −0.29 ‰, *Re* = ~2 pg/g: Dellinger et al., 2021; Miller et al., 2011) and basalt (δ^{187}Re = −0.31‰, Re = 1.1 ng/g: Wang et al., 2024) (Fig. 6b). Whilst variations in Re concentration are set by that of the deep reservoir, resulting from a contribution from seawater and/or meteoric water and basalt dissolution, δ^{187}Re values should fall in a relatively narrow range of these different sources. Our measured δ^{187}Re values in all the samples that have experienced boiling are higher than those predicted by the simple mixing calculations, suggesting that additional processes, such as degassing, secondary mineral formation, reduction and/or thiolation must have affected the liquids.

At the Reykjanes site, the two high-temperature fluid samples (RN12 and RN24) which have the same origin/reservoir did not have identical Re concentrations or Re isotopic compositions. The increased δ^{187}Re value with progressive loss of dissolved Re may be described by a Rayleigh-type fractionation:

$$\delta^{187}\mathrm{Re} = \delta^{187}\mathrm{Re}_0 + \varepsilon\ \ln(f) \qquad (2)$$

where $\delta^{187}Re_0$ represents the initial Re isotopic composition as a result of simple water-rock mixing, *f* is the fraction of Re remaining in fluids (which is proportional to Re), and ε is the Re isotope fractionation factor, derived to be −0.44 ± 0.19 ‰ based on the slope of the δ^{187}Re–ln(f) relationship for the two Reykjanes samples (Fig. 6b).

The volatility of Re is known in several magmatic systems (e.g., Bernard et al., 1990), and there is the potential for kinetic Re isotope fractionation during degassing. The theoretical maximum Rayleigh fractionation coefficient (α) during vaporization as Re_2O_7 gas can be calculated as the inverse square root of the mass of the Re isotopes ($\sqrt{481.899/485.905} = 0.9959$) (e.g., Richter et al., 2007); assuming $\alpha \approx e^{\delta^{187}Re_{vapor} - \delta^{187}Re}$, then $\delta^{187}Re_{vapor} - \delta^{187}Re \approx -4.1$ ‰. This is, however, much larger than the calculated Re isotope fractionation factor at the Reykjanes site. Our observed trend may not be explained by degassing of Re alone.

Rhenium is also known to have high affinity for sulfides (e.g., Fonseca et al., 2007). It was considered that a large proportion (up to ~61 %) of Re in hydrothermal fluids collected from the Manus Basin was present in the sulfide fraction (Miller et al., 2011). Although there is no direct observation of Re-sulfide minerals in Icelandic hydrothermal systems as yet, substantial metal-sulfide precipitation has been reported in the down-hole boiling zone and during cooling along the flow paths, notably at the Reykjanes sites (Kristmannsdóttir, 1989; Kaasalainen et al., 2015; Fowler et al., 2019). Rhenium is associated with sulfide minerals (e.g., pyrite, molybdenite) mostly as an accessory (Stein and Hannah, 2014) and, in very rare cases, as an actual Re mineral such as rheniite (Znamensky et al., 2005). Rhenium may also be found in the form as Fe(Mo, Re)S_4 as a result of co-precipitation (directly from ReO_4^-) under sulfidic conditions (Helz, 2022). Incorporation of Re into sulfide minerals can proceed rapidly (e.g., Wharton et al., 2000). No experimentally determined Re isotope fractionation factor or analysis of Re isotopic composition of sulfide materials is currently available, but kinetic effects would, in theory, enrich ^{185}Re in the 'product', leaving the residual dissolved Re isotopically heavier. Kinetic isotope fractionation showing the same direction (and similar magnitude, typically < 1 ‰) has been widely observed for other metal isotope systems such as Mo, Fe and Zn (Greber et al., 2014; Rouxel et al., 2008; John et al., 2008) during formation of sulfide minerals in global hydrothermal systems.

Additionally, reduction and/or thiolation of Re could occur in high-temperature reservoir fluids; specially, Re(VII) reduction can be facilitated in the presence of Fe(II)-bearing minerals (Kilber et al., 2024). According to the electronic structure modelling by Miller et al. (2015), the net equilibrium Re isotope fractionation factor (considering mass dependent effect, including a small nuclear volume effect) at fluid temperature (~240 to 300 °C: Fowler et al., 2019) between reduced/thiolated Re and ReO_4^- is in the range between −0.50 and +0.07 ‰; more oxidised Re compounds are predicted to be enriched in ^{187}Re. Overall, our observations at the Reykjanes sites appear to be consistent with both (i) kinetic isotope fractionation during rapid incorporation of fluid Re into sulfide minerals, and (ii) equilibrium isotope fractionation as Re is lost from the fluid via reduction/thiolation.

Similar Re removal processes can also occur at the Hellisheidi, Nesjavellir, and Svartsengi systems such that an estimated Re isotope fractionation factor (between mineral and fluid) of ~ −0.44 ‰ may be used to predict δ^{187}Re in fluids that are meteoric-sourced (and of mixed type) (Fig. 6b), although the extent and type of mineral precipitation will vary (Fowler et al., 2019). Note that as these fluids are partly modified by the influx of magmatic gases (Ármannsson, 2016), the intrinsic Re isotope fractionation may also be moderated by incorporation of relatively light Re from the steam (vapour) phase, which adds complexity. Nevertheless, as shown in Fig. 6a, these high-temperature fluids can be divided into two groups. One of these groups (from Reykjanes, Svartsengi, and Hellisheidi) has Re concentrations (1.28 to 7.06 pg/g) close to or higher than Mývatn cold groundwaters, while the other group (from Nesjavellir) has very low Re concentrations (0.61 to 0.65 pg/g). Albeit being geographically unrelated, the distinct 'groups' observed at SW Iceland support that there can be more than one hydrothermal end-member that account for the Re isotope variations in the warm Mývatn spring/groundwaters as discussed in Section 5.1. Overall, while the source of feedwater (seawater versus meteoric) and the degree of water-rock interaction primarily control the amounts of Re dissolved in reservoir fluids, loss of Re during formation of secondary reduced minerals (and possibly, during degassing) largely drives the heavy δ^{187}Re of the high-temperature hydrothermal end-members.

Additional samples collected from the Geysir geothermal field have variable Re concentrations (1.01 to 6.47 pg/g) and δ^{187}Re values (−0.23 to +0.34 ‰) (Fig. 6a). The Re concentration and δ^{187}Re value of the boiled alkaline water (GY1: 6.47 pg/g and −0.23 ‰) were respectively higher and lower compared to reservoir fluids that are meteoric sourced; additional Re may have been leached from bedrock. Simple mass balance calculation suggests this GY1 sample can be explained by addition of Re that has basaltic δ^{187}Re composition to the Nesjavellir fluids. The steam-heated acid water (GY3) is depleted in Cl (Figure S3a) due to steam condensate dilution, while degassing is also likely to occur (Kaasalainen and Stefánsson, 2012); these two processes may respectively, enrich and deplete fluid in ^{185}Re. As a fraction of Re from sediments may also be mobilized at low pH (~2.7) with unknown isotope effect, the δ^{187}Re of −0.23 ‰ and the low Re concentration (1.01 pg/g) for this acid water sample are likely not controlled by a single process. At the same area, the unexpectedly high δ^{187}Re value (+0.34 ‰) of the mixed geothermal water (GY2) may reflect similar processes as observed for the high-temperature reservoir fluids, such as incorporation of Re into secondary reduced minerals, reduction and/or thiolation. Together, these data reveal that significant Re isotopic fractionation can occur in the Earth's surficial environments, and hint at complexity in the geochemical cycling of Re.

5.3. *Implications for the global Re and Re isotope cycling*

The budget of Re in the ocean is mainly controlled by the inputs from various sources (rivers, groundwaters, hydrothermal venting) versus the accumulation of Re into marine sediments (Miller et al., 2011; Sheen et al., 2018) (Fig. 7). Whilst understanding this budget is critical for reliable application of the Re proxy to paleo studies (Crusius et al., 1996; Morford and Emerson, 1999; Calvert and Pedersen, 2007; Morford et al., 2009), recent study by Hong et al. (2024) showed that the estimated removal flux of Re (when the global shelf reductive sinks are accounted for) may be twice as much as the riverine input flux of Re (~4.3 × 10^5 mol/yr), suggesting that uncertainties remain in quantifying the sources and sinks of Re.

The only measurements for Re in hydrothermal fluids reported to date was from the PACMANUS vent field, Manus Basin (Miller et al., 2011): by incorporating dreg (sulfide) fraction into fluid composition and extrapolating to zero-magnesium, end-member Re concentrations were estimated to be 0 to 1.06 pg/g (Miller et al., 2011). This observation is consistent with Re enrichments in metalliferous sediments near the East Pacific Rise (Colodner et al., 1993) as well as in altered oceanic crust (e.g., Reisberg et al., 2008), suggesting that seafloor hydrothermal systems are a sink for seawater Re. Our measured Re concentrations in seawater-fed reservoir fluids are 3.16 to 7.06 pg/g. These lower-than-seawater values mean that Re is being removed during fluid-rock interaction at high temperature (Section 5.2). As the estimated hydrothermal removal flux of Re is three orders of magnitude lower than the riverine flux of Re to the oceans (regardless of whether fluid data from Miller et al. (2011) or in this study are used; it is, however, worth noting that given the obvious differences in pressure and temperature, the Reykjanes sites may not be analogue to the mid-ocean ridge hydrothermal systems), it is unlikely that seafloor hydrothermal venting can exert a large net impact on the seawater Re budget.

Constraining the flux and the isotopic composition of groundwater input is also of importance as groundwater discharge displays a high spatial variability and may be equivalent to as much as 25 % of the riverine water flux in some regions (e.g., Luijendijk et al., 2020). On the one hand, results from this study show that pristine Icelandic groundwater has very slightly lower dissolved Re concentration, and very slightly lower δ^{187}Re value, compared to river water (global mean, or the Mackenzie River water: Miller et al., 2011; Dellinger et al., 2021). Whether such subtle differences are controlled by lithology is not known; expanding the Re dataset to other localities is recommended for future studies. On the other hand, we show that these groundwaters could mix with compositionally distinct geothermal end-members (Figs. 4a, 6a). Recent studies on rivers draining the Tibetan Plateau suggest that geothermal waters can significantly affect the oceanic budget of some metals such as lithium and boron (Zhang et al., 2022; Xiao et al., 2023) via inputs into groundwaters and rivers. However, the very low Re concentrations in the highest temperature springs strongly indicate a Re-depleted geothermal source (Section 5.1), which may compensate any addition of Re to groundwaters from a modestly higher-Re fluid. Overall, there is no clear evidence that geothermal sources can act to modulate the possible secular changes in seawater

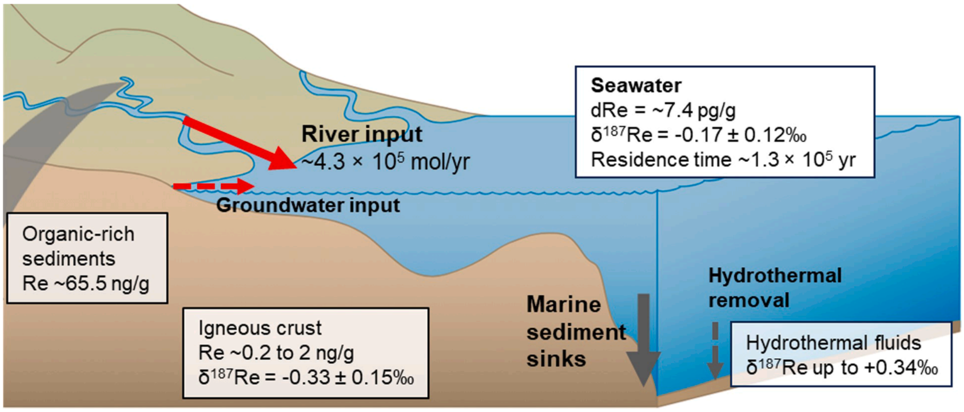

Fig. 7. Schematic illustrating potential sources and sinks of Re in the modern ocean that are explored thus far (Section 5.3). Background image courtesy of vecta.io. Dissolved riverine flux is from Miller et al. (2011), representing the major source of Re to the ocean. Seawater values are from Anbar et al. (1992) and Dickson et al. (2020). Newly estimated global shelf reductive sinks for Re (Hong et al., 2024) are comparable to previously established suboxic/anoxic sinks (Sheen et al., 2018), possibly indicating a mass imbalance of Re in the modern ocean. Note that removal of Re can also occur via hydrothermal alteration of the oceanic crust (Reisberg et al., 2008). While existing measurements on hydrothermal fluids suggest that seafloor hydrothermal systems are not a large source or sink of Re to/from the oceans, the δ^{187}Re of hydrothermal fluids is distinct from that of seawater.

δ^{187}Re caused by riverine input of Re via oxidative weathering fluxes (Dellinger et al., 2021), which may have increased over the Cenozoic due to mountain uplift and exhumation of sedimentary cover (e.g., Horan et al., 2017; Zondervan et al., 2023).

While a better understanding of the budget of Re in the ocean is clearly required, this study provides field data on Re isotopic fractionation that occurs under sulfidic/reducing conditions, furthering our understanding of Re isotopes as a tracer for redox processes operating in Earth's critical zones and potentially in ocean sediments (Miller, 2009; Miller et al., 2015; Dickson et al., 2020; Dellinger et al., 2021). Similar to Mo, Re has a long residence time and behaves conservatively in the ocean, in which the isotopic composition is a function of the relative sizes of the various input fluxes and sinks to which it is removed. Coupled Re and Mo isotope analysis may become a powerful tool for tracking and reconstructing ocean (de)oxygenation, especially for tackling intermediate redox zones where the bulk geochemical signal of Mo is controlled by multiple dissolved and solid phase sequestration pathways (e.g., Hlohowskyj et al., 2021).

6. Conclusions

This study investigates the modern-day cycling of Re isotopes with new samples collected from groundwaters and hydrothermal systems in Iceland. Rhenium is likely released from host basalts into cold groundwaters without resolvable isotopic fractionation. Groundwaters in the Mývatn area are likely influenced by two distinct hydrothermal end-members, both of which are enriched in ^{187}Re. Whilst mixing between different end-members can account for the co-variation between δ^{187}Re and δ^{98}Mo in the warm Mývatn springs, preferential removal of Re over Mo, possibly via reduction and/or degassing of Re, may have occurred. In contrast to cold groundwaters, high-temperature fluids (that have experienced boiling) collected from SW Iceland all exhibit very high δ^{187}Re values (up to +0.34 ‰) despite different types of fluid reservoirs. The degree of water-rock interaction as well as Re removal via secondary reduced mineral formation (and possibly, degassing) are thought to drive the Re elemental and isotopic variations in these fluids. Water samples collected from the Geysir geothermal field also show high but variable δ^{187}Re values, hinting at a complex combination of mixing and secondary processes operating at these sites. Results from this study confirm that seafloor hydrothermal systems are not a large source or sink of Re to/from the oceans and suggest the need for better quantifying the oceanic budget of Re through expansion of the groundwater dataset. Finally, the naturally occurring large Re isotopic fractionation (despite its small mass difference) point to the potential of using Re isotopes to track and reconstruct redox processes, which may complement the Mo isotope proxy.

CRediT authorship contribution statement

Wenhao Wang: Writing – original draft, Visualization, Investigation, Formal analysis. **Alexander J. Dickson:** Writing – review & editing, Validation, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Mathieu Dellinger:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Kevin W. Burton:** Writing – review & editing, Resources, Methodology, Investigation. **Deirdre E. Clark:** Writing – review & editing, Resources, Methodology, Investigation, Formal analysis. **Guðjón Helgi Eggertsson:** Resources, Investigation. **Íris Eva Einarsdóttir:** Resources, Investigation. **Heimir Ingimarsson:** Resources, Investigation. **Kiflom Gebrehiwot Mesfin:** Resources, Investigation. **Robert G. Hilton:** Writing – review & editing, Project administration, Investigation, Funding acquisition, Conceptualization. **Julie Prytulak:** Writing – review & editing, Project administration, Investigation, Funding acquisition, Conceptualization.

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

Data included in the table of the manuscript.

Acknowledgements

This work was funded by Natural Environment Research Council UK Standard Grant to RGH, AJD, and JP (NE/T001119). We are grateful to ÍSOR, HS Orka, Reykjavík Energy, and Umhverfisstofnun for their assistance with sample collection and generous sharing ancillary information. We thank Finnbogi Óskarsson for guidance during the preparation of this work, as well as Prof. Sigurdur Gislason for kindly providing access to laboratory space. We thank the reviewers for their constructive comments.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2024.119046.

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