Rare earth elements and yttrium in geothermal fluids

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Rare earth elements and yttrium in geothermal fluids

Abstract
The series of rare earth elements and yttrium (REY) is a useful tool in tracing the origin of fluids, which is fundamental in understanding any fluid-rock system. The suite of REY enables to study the source of fluids, the state of equilibrium in water-rock interaction, and changes of fluid composition by both precipitation of scale during ascent and by dissolution of scale particles during sampling of liquids and vapours. Knowing the amount of scale formation and the distribution of REY between liquid and scale, the REY abundance in the original fluid under bottom hole conditions can be back-calculated. Partition factors of elements between vapour and liquid increase from alkalis to earth alkaline elements to REY. Significant fractions of REY are transported by CO$_2$ rich vapour.

1. Introduction

Studies of the distribution of REY in high-temperature water-rock interaction is hampered by difficulties in sampling (i) the thermal water under source conditions and uncontaminated by surface- or groundwater, and (ii) the altered host rock in equilibrium with the fluid. One can only attempt to make the best choice with respect to the altered aquifer rocks (Möller, 2002).

Most groundwater sampling is done at 1 bar and discharge temperatures, i.e., conditions different from those at depth. For example, CO$_2$ degassing increases pH and leads to carbonate precipitation. Due to cooling, silica, sulphides, and/or various oxihydroxides flocculate, and many trace elements are sorbed or co-precipitated. Furthermore, change of pressure and temperature during ascent of water induces formation of metastable components and surface coatings, and ion exchange as a function of fluid flow. Sampling aquifer rocks is even more complicated. Most aquifers are petrologically inhomogeneous and the residence time of water is locally variable. Therefore, the rare earth elements (REE) and yttrium (henceforth combined to REY) abundance in waters never represents equilibrium sensu stricto with any sampled piece of rock suspected to represent the source rock (Möller, 2002).

The group of REY yield information on fractionation mechanisms during alteration of rocks and fluid transport, the history of rock alteration, and the state of equilibrium in water-rock interaction. Different from major components of thermal waters high fractions of many trace element such as REE and Y originate from dissolution and alteration of accessory minerals (Möller et al., 1997a; Möller, 2000; Hannigan and Sholkovitz, 2001). Only the REY patterns of waters from limestones and dolostones resemble those of the source rocks (Möller, 2002).

Distribution of REY is studied for two main purposes: (i) theoretical understanding of the systematic changes within a set of elements that are mainly trivalent and (ii) application of their fractionation as a geochemical probe to study minero-chemical processes in water-rock interaction in the Earth’s crust. The first topic is dealt with by
theoretical chemists and physicists, whereas the latter is the unique domain of geochemistry. Since it has become an easy task to determine the abundance of REY, geochemical literature is flooded by papers using REE to characterise the source and differentiation of melts and fluids. The study of REY in geothermal waters contribute to the understanding of water-rock interaction at enhanced temperatures. The knowledge of the composition of fluids and their sources is mandatory for their usage in geothermal power generation and in ore deposit research. Of particular interest are the anomalous behaving lanthanides (Ce, Eu) and Y that yield further information on process-controlling parameters.

2. Principles of rare earth element distribution

Rare earth elements and yttrium were discovered latest due to their similarity in chemical behaviour and difficulties in separating them. They represent a suite of elements of the third group in the periodic table (Fig. 1). This suite is unique in nature because

- REY are omnipresent in nature at low abundance,
- Ionic radii decrease systematically from La to Lu; this lanthanide contraction (Fig. 2) is the result of increasing number of $4f$ electrons;
- They are coprecipitated with almost all minerals except those with very small major ions in minerals like Mg$^{2+}$ and Fe$^{2+}$;
- They rarely form visible own minerals except in rare metal pegmatites and hydrothermal mineralisations associated with carbonatites.

Various processes control REY abundance in solutions:

- Solubility of REY hosting minerals and this includes REY distribution among minerals;
- Chemical complexation in solution and on surfaces;
- Distribution in the electric double layer attached to mineral surfaces;
- Processes across mineral surface.

In solution, REY undergo chemical complexation of variable strength with OH$^-$, F$^-$, HCO$_3^-$, H$_2$PO$_4^-$ etc. (Haas et al., 1995). These complexes enhance REY abundance in solution. In contrast, surface complexation reduces REY abundance in solution. In CO$_2$ rich geothermal waters, the solubility of many minerals depends on the partial pressure of CO$_2$.

Ion distribution in the electric double layer is controlled by the surface charge of the mineral. If the surfaces are negatively charged, positively charged free and complexed REY are attracted and their concentration is enhanced compared with their abundance in solution far away from the surface. Due to positively charged surfaces positively charged free and complexed REY are consequently impoverished in the electric double layer. Thus, coprecipitation with alteration minerals is less than in case of a negatively charged surface.

The distribution of REY is not homogeneous in rocks. It depends on the mineralogical composition of rocks and their state of alteration. This is shown by acidic leaching at about pH 3 (Möller and Giese, 1997). For fresh and altered felsic and mafic rocks the
leached fraction of REY after 2 and 20 hours are used to construct Fig. 3. In fresh granites the fraction of light REE is less than the heavy. In altered granite the REY are less leached than in the fresh, which means that during hydrothermal alteration REY are re-distributed. Thereafter, the light REE are significantly less leachable than the heavy ones; i.e., light REY are fixed in alteration minerals. Eu, however, is much more leachable than all the other REY. In mafic rocks REY are homogeneously distributed in

Fig. 1: Periodic table

Fig. 2: Crystallographic ionic radii as a function of atomic number. The declining trend of radii for REE is known as lanthanide contraction. Y ideally fits into the position of Ho. Open symbols represent Ce(IV) and Eu(II). For comparison, the radii of Ca$^{2+}$, Mg$^{2+}$, and Fe$^{2+}$ are given. Only Ca$^{2+}$ fits into the range of REY radii.
Fig. 3: Examples of variations of leachability of elements from fresh and altered granite (Ore Mountains, Germany) and fresh (chilled margin) and the inner part of a pillow of MOR basalt (East Pacific Rise). Details are discussed in the text.

the glassy matrix or in chilled margins. With alteration and enhanced crystallisation REY become much more leachable in short times. Very important is the fact that Eu is significantly less leachable than the other REE because it is mainly hosted by plagioclase.
2. Sampling of water

Thermal waters below 100°C are sampled directly, whereas the high-temperature fluids had to be sampled with the help of a cooling device in order to condensate the steam. The cooling device (Fig. 4) is made of stainless steel and is connected to the production lines by a flexible metal-mantled rubber tube. The liquid-steam mixture at the well head and the liquid from the cyclone separators is guided through a steel spiral which is cooled in a water tank, whereas the steam from the subsequent cyclone separator passes an additional small separator made of stainless steel and containing a package of stainless steel wool at which small droplets are forced to precipitate before cooling and condensing water from the vapour. The non-condensable gases are released to the atmosphere.

Ten litres of water or condensate are collected in polyethylene carboys under a CO\textsubscript{2} atmosphere of about 1 bar. Thereafter, the samples pass a 0.2 µm filter in order to minimise the potential dissolution of carbonate scale particles dragged along with the fluids. During filtration, 1 ml of 100 ng/g Tm spike solution and 6 M sub-boiled HCl are added to the filtrate. The Tm spike is necessary for later efficiency control of REY in the following preconcentration treatment. The acid is needed to adjust the waters to pH 2.

![Sampling device for high-temperature fluids.](image)

3. Analysis of REY

REY abundance in natural waters is in the range of nmol/kg to even below pmol/kg. Therefore, REY have to be preconcentrated prior to analysis (Shabani et al., 1992; Bau and Dulsik, 1996; Möller et al., 1998). In brief, the filtered waters are adjusted to pH 2, and, after few hours waiting, passed over a preconditioned C\textsubscript{18} Sep pak cartridge (Water
Corp. USA) at a rate of 1 litre per hour. The preconditioning of the cartridges comprises: cleaning with 10 ml 6 M sub-boiled HCl, washing with 7 ml ultra-pure water, freeing from water and loading with a liquid ion exchanger consisting of a mixture of ethylhexylphosphates.

In the laboratory, the REY loaded cartridges from the field are washed with 50 ml 0.01 M sub-boiled HCl. Thereafter, the REY are eluted by 40 ml 6 M sub-boiled HCl at a rate of 3 ml/min. The eluates are evaporated to incipient dryness and the residues dissolved in 1 ml of 5 M sub-boiled HCl and spiked with a Ru-Re mixture which is later used for corrections of the internal drift of response factors in inductively coupled plasma mass spectrometry (ICP-MS) measurements if necessary. REY are not fractionated by the applied preconcentration conditions.

The spectra are routine corrected for interferences of molecular ions with the wanted mono-charged ions of the REY (Dulski 1994). In addition, $^{139}$La$^+$ had to be corrected for the interference by $^{123}$Sb$^{16}$O$^+$ because Sb is not quantitatively separated from REY by the described ion exchange procedure (Möller et al., 2003).

High REY abundances are precise within ±5 %, whereas the lowest ones may vary by a factor of two due to the uncertainties related to interferences and nearness of limits of detection. All reported data are 3 times above the limits of detection.

5. Presentation of data

When plotting the abundance of REE towards the atomic number a zigzag or saw-teeth like curve is obtained (Fig. 5a). Such abundance curves are difficult to compare, in particular, if individual elements behave anomalously. For that reason, Coryell et al. (1963) suggested to normalise the REY abundance by that in C1-chondrite (Table 1; Anders and Grevesse, 1989), which represented the least fractionated REY abundance in matter known at that time (Fig. 5b). Normalisation yields smooth REY patterns. In the meantime different other materials have been proposed for normalising REY abundances such as the Post-Achaean-Australian-Shale, PAAS (Table 1; McLennan, 1989).

Fig. 5: Normalisation of REE and Y abundance. In (a) REY abundances of C1-chondrite (Anders and Grevesse, 1989) and Post-Achaean-Australian Shale (PAAS; McLennan 1989) are given. In (b) PAAS is normalised by C1-chondrite.
1989), or even the source rocks of waters. Normalisation does not alter the abundance, it only visualises changes of trends with respect to the normalisation matter and depicts anomalously enriched or depleted elements. Of course, the patterns look different when normalised to different materials (Fig. 6). If we normalise all waters with respect to one reference material, the resulting curves are easier to compare than the corresponding tabulated data.

As shown in Fig. 7, REY patterns show a variety of trends: they increase or decrease from La to Lu or can even show a maximum or minimum. The deviation from a flat trend is termed fractionation with respect to the normalisation material. Fractionation always occurs, if either light or heavy REE show a special affinity to minerals by which

![Fig. 6: Normalisation of Kizildere high-enthalpy fluid by C1-chondrite and PAAS.](image)

**Table 1: Rare Earth and Y abundance in C1-chondrites and Post Achaean Australian Shale (PAAS)**

<table>
<thead>
<tr>
<th>Element</th>
<th>C1-chondrite pmol/kg</th>
<th>PAAS pmol/kg</th>
<th>C1-chondrite µg/g</th>
<th>PAAS µg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>1.69E+06</td>
<td>2.75E+08</td>
<td>0.235</td>
<td>38.2</td>
</tr>
<tr>
<td>Ce</td>
<td>4.30E+06</td>
<td>5.68E+08</td>
<td>0.603</td>
<td>79.6</td>
</tr>
<tr>
<td>Pr</td>
<td>6.32E+05</td>
<td>6.27E+07</td>
<td>0.089</td>
<td>8.83</td>
</tr>
<tr>
<td>Nd</td>
<td>3.13E+06</td>
<td>2.35E+08</td>
<td>0.452</td>
<td>33.9</td>
</tr>
<tr>
<td>Sm</td>
<td>9.77E+05</td>
<td>3.69E+07</td>
<td>0.147</td>
<td>5.55</td>
</tr>
<tr>
<td>Eu</td>
<td>3.68E+05</td>
<td>7.11E+06</td>
<td>0.056</td>
<td>1.08</td>
</tr>
<tr>
<td>Gd</td>
<td>1.25E+06</td>
<td>2.96E+07</td>
<td>0.197</td>
<td>4.66</td>
</tr>
<tr>
<td>Tb</td>
<td>2.27E+05</td>
<td>4.87E+06</td>
<td>0.036</td>
<td>0.774</td>
</tr>
<tr>
<td>Dy</td>
<td>1.50E+06</td>
<td>2.88E+07</td>
<td>0.243</td>
<td>4.68</td>
</tr>
<tr>
<td>Y</td>
<td>1.75E+07</td>
<td>3.04E+08</td>
<td>1.56</td>
<td>27.0</td>
</tr>
<tr>
<td>Ho</td>
<td>3.40E+05</td>
<td>6.01E+06</td>
<td>0.056</td>
<td>0.991</td>
</tr>
<tr>
<td>Er</td>
<td>9.50E+05</td>
<td>1.70E+07</td>
<td>0.159</td>
<td>2.85</td>
</tr>
<tr>
<td>Tm</td>
<td>1.42E+05</td>
<td>2.40E+06</td>
<td>0.024</td>
<td>0.405</td>
</tr>
<tr>
<td>Yb</td>
<td>9.42E+05</td>
<td>1.63E+07</td>
<td>0.163</td>
<td>2.82</td>
</tr>
<tr>
<td>Lu</td>
<td>1.37E+05</td>
<td>2.47E+06</td>
<td>0.024</td>
<td>0.433</td>
</tr>
</tbody>
</table>
they are hosted in nature. The fractionation can be the result of a fractional release from host minerals or fractionated incorporation in alteration minerals (including scale formation in boreholes).

Fig. 7: C1-chondrite normalised REY patterns of various thermal fluids with anomalies. (a) Water from limestone of Pamukkale/Turkey (35°C) and water from carbonate rocks near Kula/Turkey (19°C; Möller et al., in press); bine from Tyro sub-basin in the Mediterranean Sea at 3200 (16°C; Bau et al., 1997); (b) Mediterranean seawater from 3200 m depth (Bau et al., 1997); water from alkaline Lake Van/Turkey (Möller and Bau, 1993); water from Jachymov, Krusne hory granite, Czech Republic (34°C; Möller et al., 1998); (c) waters from Slavkovsky-les granite and Duopovske hory basalt, Kyselka, Czech Republic (Möller et al., 1998); (d) waters from limestones/evaporite sequences and phyllites, Tuscany, Italy (200°C; Möller et al. 2003); average of 21 water samples from mica schists and marble, Kizildere, Turkey (190°C; Möller et al., in press).
6. Anomalous behaviour of Ce, Eu and Y

Conventional definition of anomalies are

\[
\frac{Ce}{Ce^*} = \frac{(La_N + Pr_N)}{2Ce_N}
\]

(1)

\[
\frac{Eu}{Eu^*} = \frac{(Sm_N + Gd_N)}{2Eu_N}
\]

(2)

Here * indicates the geogene abundance interpolated between the two adjacent elements in the series. The index \( N \) denotes normalisation.

On a logarithmic scale as used for presentation of REY patterns (Fig. 7), deficits of Ce or Eu show up as negative anomalies (logarithms of Ce/Ce* or Eu/Eu* ratios <1 are negative). Excess of Eu or Ce yield positive anomalies.

Negative Ce anomalies are quite common in oxygen rich surface waters. For instance, seawater, oxygen-rich river- and karst waters are characterised world-wide by negative Ce anomalies (Fig. 7a). Bau (1999) and Kawabe et al. (1999) showed experimentally that Ce anomalies develop during aging of FeOOH precipitates. Starting with undifferentiated scavenging of all REE and Y, most of these elements are released during aging, only Ce is retained as Ce(IV) leading to the positive Ce anomaly in the final precipitate and a corresponding negative one in waters. For instance, the strongly negative Ce anomaly of the thermal water of Pamukkale (Fig. 7a) with Eh values of about +400 mV may be due to long residence time of this water in the karst aquifer, in which FeOOH precipitation occurs along with dissolution of Fe-bearing carbonates. In contrast, waters from most igneous and metamorphic rocks yield low Eh values and, therefore, FeOOH does not precipitate and negative Ce anomalies cannot develop.

Positive Ce anomalies are achieved, if Ce-enriched FeOOH coatings come into contact with chemically reducing fluids. At various places in marine and lacustrine systems strongly reducing environments exist in the lower water column, in which sedimenting particles coated by FeOOH are re-dissolved such as in the high-salinity brine of the Tyro sub-basin in the Mediterranean Sea (Fig. 7b) (Bau et al., 1997).

Another process is carbonate complexation of Ce(VI) in alkaline lakes such as Lake Van, Turkey, with pH of 9.5 (Fig. 7b) (Möller and Bau, 1983).

Among the studied waters from felsic rocks, positive Ce anomalies were found in the thermal water from Jachymov, Krusne hory, Czech Republic (Fig. 7b). The granite of Jachymov has been altered along with the formation of post-Variscan uranium mineralization. Since U is only mobilised by oxidising fluids, it is plausible that also Ce was partially oxidised and fixed at mineral surfaces of the altered granite. The present-day water from the bleached Jachymov granite is chemically reducing and contains Fe^{2+}. Thus, the once fixed Ce(VI) is leached in addition to the Ce fraction from dissolving minerals.

Strongly positive Eu anomalies are observed in the high-temperature, acidic vent fluids of black smokers (Fig. 7c) and the high-temperature fluids (HTF) of the Monte Amiata geothermal field (Fig. 7d). Significantly positive anomalies always occur at
temperatures above 250°C (Mölter, 2000). This coincides with two features: (i) all high-temperature fluids are chemically reducing, and (ii) calculation (Sverjenski, 1984) and experiments (Bilal, 1991) showed that Eu is increasingly present in the divalent state at temperatures above about 250°C. In alteration reactions, Eu(II) behaves different from Eu(III) and all the other REY. The trivalent REE are coprecipitated with alteration minerals, whereas the big Eu(II) (Fig. 2) is rejected and, therefore, mainly sorbed onto mineral surfaces. This fraction of “loosely-bound” Eu onto mineral surfaces, often referred to as “excess Eu”, is more easily leached from rocks by percolating water than the lattice-bound REE, although at low temperatures all leached Eu is trivalent. Thus, the either positive or negative Eu anomalies of fluids inherited from their source rocks are either enhanced or diminished by the excess Eu, respectively.

The most important source of an inherited Eu anomaly is the alteration of feldspars, particularly plagioclase. Since most igneous feldspars show a positive Eu anomaly, their dissolution or alteration yields fluids with positive Eu anomalies. For instance, the high temperature alteration of plagioclase (>250°C) is considered as the source of the strongly positive Eu anomalies in black smoker fluids (e.g., Klinkhammer et al., 1994). In contrast to plagioclase, alkali feldspars are much more stable in contact with hydrothermal fluids and, therefore, their contribution of Eu is less than that of plagioclase. Separated biotite from felsic rocks, which normally hosts numerous tiny solid inclusions of accessory minerals, shows strongly negative Eu anomalies, which result from the many solid inclusions. Pure biotite is low in REY and shows negligible Eu anomalies (Bea et al., 1994). When biotite in felsic rocks is chloritised, the fluid inherits the abundance distribution of REY in “biotite” and its negative Eu anomaly. Because the excess Eu from the intergranular space of rocks is leached faster than REY from minerals, the source-rock-normalised REY patterns of water loose the initially positive Eu anomaly with time. This is the reason, why many thermal and high-temperature waters only show insignificant Eu anomalies (Fig. 7d). This is expected in systems that reached static equilibrium. The superheated steam from Larderello/Italy (about 200°C) does not show a positive Eu anomaly, whereas fluids from the young Monte Amiata geothermal field/Italy (about 300°C) are marked by Eu and Y anomalies. These young boreholes produce from an aquifer which has not yet reached static equilibrium under conditions of steam production.

The Y anomaly is defined by the Y/Ho ratio. Under igneous conditions Y behaves precisely like Ho (Bau and Dulski, 1965). In aqueous systems, Y displays a different behaviour, which may be related to small differences in solubility products of the hydroxides (Diakonov et al., 1998). In migrating fluids, however, the small dissimilarity of sorption onto mineral surfaces, controlled by surface complexation yields Y-Ho fractionation. Different from anomalous Eu, the Y/Ho ratio is not dependent on temperature. In some groundwaters and thermal waters Y is enriched compared to Ho (see Y and Ho in Fig. 7). This anomaly is only acquired, whilst the rock is not in equilibrium with the migrating water. If such a process lasts long enough, static equilibrium is reached and Y anomalies (like Eu anomalies) vanish. Most waters, however, exhibit acquired Y anomalies. Y in the steam of the long-time exploited Larderello geothermal field (Tuscany, Italy) behaves not anomalously, whereas in the
new production field of Monte Amiata (Tuscany, Italy) Y is leached in excess indicating that static equilibrium is not established.

7. Applications of REY patterns as a geochemical probe

7.1 THERMAL WATERS

Thermal waters show variable chemical composition because they originate from various types of aquifer rocks with different suites of REY-bearing accessory minerals. Therefore, thermal waters from felsic and mafic rocks show different types of REY patterns normally with positive Y anomalies (Fig. 7c). In particular, thermal waters from granites show negative Eu anomalies.

Fig. 8: Survey of C1-chondrite normalised thermal waters along the Lake Kinneret - Jordan Valley - Dead Sea – Arava Valley transform fault (Möller et al., 2003). The thermal groundwaters are grouped according to their REY patterns, which characterise the replenishment areas. Irrespective other rocks or sediments in contact with groundwater, the original REY patterns are not changed significantly. They can be used for establishing a regional hydrostratigraphy.
Rocks or sediments, in which the water-rock interaction occurs and REY are leached, may not be the same as the ones from which the waters are finally recovered. In general, REY are only negligibly leached, in other words they are highly retained by minerals (Möller, 2002). If such waters pass other permeable rocks or sediments, they often imprint their REY abundance onto the new environment, i.e., along the pathways of fluids the REY composition resembles that of the primary source rocks. This is why REY keep in memory from which type of rock they are derived, e.g., the interaction of meteoric water with rocks of the recharge area occur.

Waters from sedimentary rocks are highly variable depending on the mineralogical composition of the recharge areas. For example, in Israel and Jordan the thermal groundwaters from limestones, basalts and sandstones of different geologic formations can be differentiated by their REY patterns (Fig. 8). Here, REY patterns can be used as a tool in hydrostratigraphy. In some cases, the chemically derived hydrostratigraphy is

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Fig. 9: Sketch map of W-Anatolia/Turkey, southeast of Izmir, with the Bozdag Mountains and the Büyük (BMG) and Küyük Menderes (KMG) grabens, and the Gediz graben (GG) (a). The geothermal fields are given by bold triangles. Open triangles indicate thermal springs: 1=Tekkehamam; 2= Babacik; 3= Ujuzhamami; 4= Yenice; 5= Gölemezli; 6= Pamukkale; 7= Bozköy; 8= Sazliköy; 9= Gümüsköy. (b) Generalised drilling log of Kzildere area.
not identical with the assumed source lithology or aquifer according to geologic knowledge (Möller et al., 2003).
The Na-HCO$_3$ type of waters from the thermal springs of Gölemezli, Tekkehamam, Babacik, and Yenicekent in Turkey occur in the Neogene sediments and are located along faults of the northern and southern flanks of the Büyük Menderes graben, W Anatolia (Fig. 9). These waters are carbonate-rich and travertine forms at natural discharges. The REY patterns (Fig. 10b) prove that the waters originate from Palaeozoic mica schist intercalated with marble which is evident by comparison of their patterns with those of the fluids from the Kizildere boreholes (Fig. 7d). The waters from Yenice (Fig. 10a), Gümüsköy and Bosköy (Fig. 10c) are different from those near Kizildere (Fig. 10b). They are strongly affected by REY exchange with clay minerals. Although
discharging along the same fault as the Yenice, the water from Pamukkale is from another source. It originates from Tertiary limestone and is high in oxygen, i.e., it does not deeply percolate rocks before discharging (Möller et al., in press).

7.2 HIGH-TEMPERATURE FLUIDS
The high-temperature areas of Kizildere/Turkey, Monte Amiata/Italy and Larderello-Travale/Italy produce steam has a very high initial gas/liquid ratio and is characterised by high CO$_2$ contents. These geothermal fields are exploited for electric power generation.

7.2.1 Geological background
W Anatolia/Turkey: The Menderes Massif (Fig. 9) is the oldest rock assemblage of the Anatolian Continent and comprises high-grade gneisses and schists overlain by low-grade schist, marble, phyllite, metapluxonites and metasedimentary rocks associated with recrystallised limestones. The Miocene sedimentary rocks are succeeded by mega-sequences of clastic, carbonate- and organic-rich sedimentary rocks. The sedimentary facies mainly occur as alluvial fans, fluvial carbonate mudflats and ephemeral shallow freshwater carbonate lake deposits. Volcanic facies and borate deposits interfinger these sedimentary sequences. The Pliocene sedimentary succession resembles in composition the underlying Miocene.

Grabens developed to the N and S of the Bozdag Horst (Fig. 9). Due to rapid uplift, high seismicity, and erosion very thick and coarse-grained alluvial and fluvial Pliocene to Quaternary sediments accumulated in the Gediz-, Kücük Menderes-, and Büyük Menderes grabens. In W Anatolia, the Early-Middle Miocene shoshonitic and ultrapotassic-lamproitic volcanism is considered to be related to the oceanic subduction that developed in the Aegean area after the Cretaceous–Eocene collision of the Sakarya and Anatolian continents (Francalanci et. al., 2000). A second alkaline volcanic phase started in the Middle Miocene and increased volumetrically with time.

Most of the geothermal systems are bound to intersections of the youngest E-W trending grabens and older NW-SE and NE-SW striking faults. The Kizildere Geothermal Field is part of the enormous Denizli-Buldan-Sarayköy geothermal area near the junction of the Gediz- and the Büyük Menderes grabens (Fig. 9). At the geothermal plant of Kizildere, eight wells, cased to depths of 500 to 1000 m, produce extremely CO$_2$-rich fluids from the crystalline basement with bottom hole temperatures up to 240$^\circ$C and pressures ranging from 50 to 90 bar. Under bottom hole conditions the fluids contain about 0.2 to 0.4 mol of dissolved CO$_2$ per kg fluid (Satman et al., 1999). The exsolution of CO$_2$ starts at approximately 500 m below surface and a Sr-rich carbonate-silica scale precipitates. Numerous thermal springs occur in the Kizildere Geothermal Field.

In the Büyük Menderes graben there are two other geothermal fields in the state of exploration: Salavatli and Germencik. Exploration wells have been drilled in the Salihli Geothermal Field, Gediz graben, through the Miocene-Pliocene conglomerate,
Fig. 11: Geologic sketch map of Tuscany/Italy showing the two important geothermal areas of Larderello-Travale and Monte Amiata. Heat flow isolines are shown. The actual heat flow gradient does not reflect a monotonous decrease of the temperatures from the Monte Amiata volcano outwards, but of the heat supplied from the much larger magma chamber.
sandstone, mudstone, limestone and tuff into the Paleozoic schists, quartz schists, micaschists and marbles of the Menderes Massif. The thermal water is supplied to spas. The Kula geothermal field is located on a block of crystalline rocks east of the Gediz graben. As the youngest volcanics of Western Anatolia, the Kula volcanics are Na-dominant in character, while all the former volcanic series of Western Anatolia are K-dominant.

Tuscany/Italy: The geothermal area of Larderello-Travale and Monte Amiata (both Central Italy, Fig. 11), are well known for their many fumaroles and for the use of the high-temperature fluids (HTF) for electricity generation and domestic heating. The area of Larderello is the largest geothermal anomaly in Italy with a maximum thermal heat flow of more than 600 mW/m² (Fig. 11). The large geothermal anomalies of Tuscany are produced by a granitic batholith which intruded 3.5 Ma ago (Batini et al., 1985). The roof of the pluton is defined by the so called K horizon at about 3 to 6 km depth. This horizon is characterized by a very low acoustic impedance. The petrologic interpretation of the geophysical data suggests that it is a strongly fractured basement unit of some hundreds of meters in thickness impregnated with high-temperature and high-pressure fluids.

HTF is produced from drill holes over a large depth interval that tap more than one lithology. The geothermal wells penetrate both the Upper Triassic evaporites of the Tuscan nappes and the Carboniferous phyllitic series. Thus, two types of fluids are produced with different REY abundances and chemical composition. Until 1930, the high boron contents of the hot springs has been the basis for boric acid production by a company founded in 1808 by the industrialist Francesco Larderel. At Monte Amiata numerous Hg mineralisations cluster, whereas the Sb mineralisations are located at greater distance. A zonal distribution of the mineralisation centred around the Monte Amiata volcano is not observed. It is supposed that both types of mineralisation are related to the Monte Amiata volcanism. Until the 1960ties, the Monte Amiata mining district was the world’s second important mercury producer (Möller et al., in prep.).

7.2.2 REY in liquid and vapour.
Liquids and steam coexist in high-temperature fluids. Steam is an aerosol consisting of fine droplets of liquid and water-saturated vapour containing besides H₂O non-condensable gases under surface conditions. On a H₂O-free basis, the non-condensable fraction consists mainly of CO₂. The rather large variability in the non-condensable gas composition of the HTF is considered to be typical of gases originating from different sources at shallow depth (Gianelli and Calore, 1996).

The REY patterns of liquids and vapours from the Anatolian and Tuscan geothermal fields are shown in Figs. 12 and 13, respectively. For each of the geothermal fields most of the patterns are subparallel. In Fig. 12 individual REY patterns for well KD13/Kizildere are given in thin lines in order to visualise the high scatter of patterns at a given locality during the years of sampling. The REY patterns of liquids from Kizildere and Larderello show small negative Eu anomalies but no Ce and Y anomalies. Only the liquids from Monte Amiata show Eu and Y anomalies. The small negative
Table 2: Rare earth abundance in high-temperature liquids from the Larderello-Travale-, Monte Amiata-, and Kizildere geothermal fields.

<table>
<thead>
<tr>
<th>Source rock</th>
<th>Limestone/ evapones</th>
<th>Phylite</th>
<th>Limestone/ evapones</th>
<th>Phylite</th>
<th>Mica schist with intercalated marble</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carboli A</td>
<td>Radi-</td>
<td>PC34A + PC16bsA</td>
<td>PC33A + PC36</td>
<td>KD13/97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>condoli</td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Number of samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>125</td>
</tr>
<tr>
<td>Pressure bar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.02</td>
</tr>
<tr>
<td>Na mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.1</td>
</tr>
<tr>
<td>Y pmol/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>Sm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.13</td>
</tr>
<tr>
<td>Eu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.10</td>
</tr>
<tr>
<td>Y/Ho molar ratio</td>
<td>72</td>
<td>54</td>
<td>109</td>
<td>96</td>
<td>57</td>
</tr>
</tbody>
</table>

Table 3: Rare earth abundance in vapours from the Larderello-Travale-, Monte Amiata-, and Kizildere geothermal fields. Yearly analyses are given for Kizildere well KD13.

<table>
<thead>
<tr>
<th>Source rock</th>
<th>Larderello-Travale</th>
<th>Monte Amiata</th>
<th>Kizildere</th>
<th>Kizildere best values: Fig. 14b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well name</td>
<td>Carboli A</td>
<td>Radicondoli</td>
<td>PC34A</td>
<td>PC27B</td>
</tr>
<tr>
<td>Limestone/ evapones</td>
<td>Phylite</td>
<td>Limestone/ evapones</td>
<td>Phylite</td>
<td>Mica schist with intercalated marble</td>
</tr>
<tr>
<td>Number of samples</td>
<td>125</td>
<td>-</td>
<td>200</td>
<td>267</td>
</tr>
<tr>
<td>Pressure bar</td>
<td>-</td>
<td>-</td>
<td>18</td>
<td>22</td>
</tr>
<tr>
<td>Na mg/L</td>
<td>0.05</td>
<td>0.2105</td>
<td>0.17</td>
<td>0.135</td>
</tr>
<tr>
<td>Ca</td>
<td>0.034</td>
<td>0.008</td>
<td>&lt;0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Y pmol/L</td>
<td>0.958</td>
<td>1.452</td>
<td>1.283</td>
<td>0.574</td>
</tr>
<tr>
<td>Sm</td>
<td>0.581</td>
<td>1.643</td>
<td>1.770</td>
<td>1.780</td>
</tr>
<tr>
<td>Eu</td>
<td>1.624</td>
<td>3.299</td>
<td>2.408</td>
<td>1.570</td>
</tr>
<tr>
<td>Y/Ho molar ratio</td>
<td>33</td>
<td>34</td>
<td>34</td>
<td>34</td>
</tr>
</tbody>
</table>
Fig. 12: C1-chondrite normalised REY patterns high-temperature fluids from Kizildere/Turkey (a), Larderello-Travale/Italy (b), and Monte Amiata/Italy (c). Figures attached to names indicate year of sampling.

Eu anomalies in waters from Kizildere, Salavatli and Germencik are inherited from mica schists (Fig. 14).

Among the Palaeozoic rocks from Turkey, the gneisses are lower in LREE and show more negative Eu anomalies than the mica schists. The REY patterns of the Pliocene shales and limestones resemble those of the Palaeozoic mica schists. The Tertiary limestones of the Kizildere and Pamukkale areas and the Palaeozoic Kula marble are the
lowest in REY among the studied rocks. The Kula marble differs from the Tertiary limestones by both strongly negative Ce and positive Y anomalies. The REY abundance

<table>
<thead>
<tr>
<th>Region</th>
<th>Larderello-Travale region</th>
<th>Monte Amiata</th>
<th>Kizildere region</th>
<th>Kula</th>
<th>Pamukkale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geologic Formation</td>
<td>Palaeozoic</td>
<td>Recent scale</td>
<td>Palaeozoic</td>
<td>Tertiary</td>
<td>Recent</td>
</tr>
<tr>
<td>Rock type</td>
<td>Phylite Limestone</td>
<td>Limestone</td>
<td>Gneiss</td>
<td>Shale Limestone</td>
<td>Travertine</td>
</tr>
<tr>
<td>Number of samples</td>
<td>(2)</td>
<td>(3)</td>
<td>(2)</td>
<td>(4)</td>
<td>(3)</td>
</tr>
<tr>
<td>CaO %</td>
<td>n.d.</td>
<td>24.6</td>
<td>54</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>Y</td>
<td>24.6</td>
<td>9.1</td>
<td>37.9</td>
<td>15.6</td>
<td>21.5</td>
</tr>
<tr>
<td>La</td>
<td>34</td>
<td>16.8</td>
<td>54</td>
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<td>2</td>
</tr>
<tr>
<td>Ce</td>
<td>9</td>
<td>23.1</td>
<td>9.55</td>
<td>13.60</td>
<td>9.93</td>
</tr>
<tr>
<td>Pr</td>
<td>9</td>
<td>2.3</td>
<td>9.1</td>
<td>9.1</td>
<td>9.1</td>
</tr>
<tr>
<td>Nd</td>
<td>31</td>
<td>9.6</td>
<td>11.0</td>
<td>39.4</td>
<td>11.0</td>
</tr>
<tr>
<td>Sm</td>
<td>5.9</td>
<td>2.7</td>
<td>3.58</td>
<td>5.68</td>
<td>2.80</td>
</tr>
<tr>
<td>Eu</td>
<td>1.2</td>
<td>0.8</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Gd</td>
<td>3.5</td>
<td>3.1</td>
<td>4.61</td>
<td>4.61</td>
<td>4.61</td>
</tr>
<tr>
<td>Tb</td>
<td>0.80</td>
<td>0.5</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Dy</td>
<td>4.7</td>
<td>2.5</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>Ho</td>
<td>0.90</td>
<td>0.5</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Tm</td>
<td>0.38</td>
<td>0.2</td>
<td>0.71</td>
<td>0.71</td>
<td>0.71</td>
</tr>
<tr>
<td>Yb</td>
<td>2.4</td>
<td>1.1</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Lu</td>
<td>0.37</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Y/Ho molar ratio</td>
<td>51</td>
<td>62</td>
<td>58</td>
<td>63</td>
<td>57</td>
</tr>
</tbody>
</table>

Fig. 13: C1-chondrite normalised REY patterns of condensates from averaged vapours. In Tuscany, Italy, Carboli and PC34 and PC16 wells produce from limestones, whereas PC16 and PC36 wells produce from phyllites (Möller et al., 2003). KD wells refer to Kizildere, Turkey. The average of 17 condensates from Kizildere is given as bold line.
of the ubiquitous travertines are similar to those of the local limestones. The REY patterns of the various high-temperature carbonate scales from Kizildere show much lower REY abundances than sedimentary carbonates and rarely anomalies. The absence

Fig. 14: C1-chondrite normalised REY patterns of representative host rocks of the reported high-temperature fluids, travertines and scales.
of significant Y anomalies in the waters indicates that sorption of REE and Y is either in static equilibrium with the leached rocks or the waters migrate on fractures and not in pores. Both arguments are consistent with the high discharge rates at Kizildere of about $2.10^5$ kg/h of each well. Some of the scatter of the Y/Ho atomic ratios (Table 3) is attributed to uncertainties of the low Ho abundance. For the well head fluids the atomic Y/Ho ratios are $61 \pm 8$. The Y/Ho ratios of $55 \pm 2$ of the condensates (Table 4) are comparable with those of liquids and the scales (Table 5). All ratios are similar within their uncertainties and comparable with the chondritic atomic ratio of $52 \pm 5$ (Bau 1996), i.e. no fractionation. The Y enrichment in the fluid and their source rocks (Table 5) is minor, i.e. REY contribution from marble (Table 4) is negligible.

7.2.3 Selection of best analyses

REY abundance in waters from each geothermal water is highly variable with time (Table 2, Fig. 12). Although the efficiency of REY preconcentration is between 95 and 106%, the REY abundances in water from each well possibly varies due to:

(i) Compositional variations in the original fluid resulting from leaching of inhomogeneously distributed REY-bearing components;
(ii) Variability of scale formation and associated coprecipitation of REY;
(iii) Uncontrollable liquid/steam ratio during sampling;
(iv) Contamination by dissolution of scale particles dragged along with the flashing fluids.

As a consequence of variable REY abundance in liquids, the REY abundance in vapours must also be variable (Table 3; Fig. 13).

Plots of the REY/Ca ratios vs. Ca contents of all Kizildere liquids indicate two different trends and a wide spread of Ca contents (Fig. 15a). The extrapolated lowest Ca content is 0.024 mmol/kg at 190°C in agreement with Table 2. This content is considered to be nearest to calcite equilibrium at flashing temperature, whereas higher Ca contents are produced by dissolution of scale particles dragged along with the flashing fluid, which dissolve at low temperature in the sampled liquids. The trend to high REY/Ca ratios

![Figure 15](image)

Fig. 15: allows to find the least contaminated values for Sm and Gd in liquid and vapour. These data are used to select the best analyses among all performed. For Kizildere these data sets are given in Table 3 and 4 as “best values”, respectively.
results from local involvement of minerals with enhanced REY abundance. Water-rock interaction does not yield constant composition of fluids with time (Middlesworth and Wood, 1998) as can be seen from well Carboli A in the Larderello- and well KD13 in the Kizildere geothermal field (Table 2). The trend to high REE/Ca ratios is also superimposed by dissolution of scale particles. The trend of slightly declining REY/Ca ratios, caused by dissolution of scale particles in the sampled fluid, results from eqs. (3-6) when inserting $\beta=2.7 \times 10^{-9}$ which characterises scale carbonates (Table 4). The steep trend is caused by $\beta=3 \times 10^{-6}$ which is characteristic for dissolution of limestones and marbles (Table 4).

$$\left( \frac{\text{REY}}{\text{Ca}} \right)_{\text{measured}} = \frac{[\text{REY}]_{\text{solution}} + [\text{REY}]_{\text{solid}}}{[\text{Ca}]_{\text{solution}} + [\text{Ca}]_{\text{solid}}}$$  \hspace{1cm} (3)$$

$$[\text{Ca}]_{\text{measured}} = [\text{Ca}]_{\text{solution}} (1 + \varepsilon)$$  \hspace{1cm} (4)

with

$$\text{REY}_{\text{solid}} = \beta \text{Ca}_{\text{solid}}$$  \hspace{1cm} (5)

$$\varepsilon = \left( \frac{[\text{Ca}]_{\text{dissolved}}}{[\text{Ca}]_{\text{solid}}} \right) = \frac{\frac{\text{REY}}{\text{Ca}}_{\text{solution}} - \frac{\text{REY}}{\text{Ca}}_{\text{measured}}}{\left( \frac{\text{REY}}{\text{Ca}}_{\text{measured}} \right) - \beta}$$  \hspace{1cm} (6)

The data points of the condensates follow a hyperbolic trend (Fig. 15b). High REY/Ca ratios are obtained when Ca is low and vice versa. This is simply a plot of $1/\text{Ca}$ vs. $\text{Ca}$ multiplied by an abundance of Sm and Gd in vapours ranging from 0.04 to 0.10 pmol/kg. If only few analyses are available, the described method cannot be applied. The intersections of the vertical and horizontal trends define the best analyses, lowest in both Ca and REE. With the help of Sm and Gd the best REY analyses are selected among the measured ones.

### 7.2.3 Element partition between liquid and vapour

Apparent partition factors between vapour and liquid, $^{\text{app}}{D_L}$, are estimated according to eq.(8) and are shown in Fig. 16.

$$^{\text{app}}{D_L} = \frac{E_l \text{ vapour}}{E_l \text{ liquid}}$$  \hspace{1cm} (7)

Although the patterns of $^{\text{app}}{D_L}$ (REY) are “noisy”, they show a slight tendency to decrease from light to heavy REY in these CO$_2$ dominated systems at temperatures ranging from 140 to 200°C and pressures from 4 to 20 bar. In contrast to REY, Na$^+$ and K$^+$ yield partition coefficients below 0.005, Cl$^-$ about 0.03. Ca$^{2+}$ is highly varying and ranges from 0.01 to 0.3. The apparent vapour-liquid partition coefficients of mono-, di-,
and trivalent ions rank in the series $\text{NH}_4^+ > \text{REY} > \text{Mg} > \text{Ca} > \text{Na}$ (Möller et al., 2003). Excepting $\text{NH}_4^+$, this series suggests that the tendency to form neutral species increases with increasing charge, at least under the PTX conditions of the studied vapour systems. $\text{NH}_4^+$ is always enriched in the vapour. Boron stays preferably in the liquid as boric acid, whereas sulphur (mainly $\text{H}_2\text{S}$) partitions into the vapour.

The REY fractionation in the CO$_2$ rich natural systems contrasts experimental results of Shmulovich et al. (2002) reported increasing $D^V_L(\text{REY})$ from La to Lu in highly acidic NaCl and CaCl$_2$ systems. REY distribution in both systems was alike. Thus a chloride and bicarbonate dominated systems behave differently with respect to REY partition.

### 7.2.5 REY distribution between scale and liquid

The CI-chondrite normalised REY patterns of scales formed at 190°C from Kizildere is slightly higher than that formed at 140°C, but both show no anomalous Eu behaviour (Fig. 16). Compared with the small negative Eu anomaly of the host rocks (mica schist with intercalated marble), Eu is slightly enhanced in scale. This is due to the original high temperatures of the fluids at their origin, where Eu(II) is leached. Carbonate formed at low $P_{\text{CO}_2}$ but high pH of about 9 in the waste water ditch is low in REY because of carbonate complex formation. In contrast, travertine and limestone, formed at surface temperatures, are higher in REY by two orders of magnitude (Fig. 14). Relating the REY/Ca ratios of the liquids to the corresponding ratios of scales (eq.8), $K_{\text{scale}}^{\text{app}}$ are obtained. The distribution factors are termed “apparent (app)” because equilibrium cannot be proved for the dynamic system.

![Graph showing averaged apparent partition coefficients](image-url)
The patterns $^{app}K_{d_{\text{scale, liquid}}}$ (Fig. 17) slightly decreases from La to Lu and are strongly dependent on temperature. In all $Kd$ patterns Y behaves anomalously because it prefers to stay in the aqueous phase. At 190°C, REY are slightly less incorporated than at 140°C. Thus, REY/Ca ratio increases in hydrothermal fluids, when carbonates precipitate during loss of CO$_2$ and cooling.

Fig. 16: Averaged apparent distribution coefficients $^{app}K_{D_{\text{scale, liquid}}}$ for the geothermal systems of Monte Amiata/Italy and Kizildere/Turkey based on data in Tables 2, 3 and 4.

7.2.6 Ca and REY contents in original fluids under bottom-hole conditions
The best data sets or average fluid composition of each geothermal field is used to estimate the corresponding total dissolved Ca and pH under source rock conditions by applying the PHREEQC program (Parkhurst and Apello, 1999). For instance, the amount of Ca in the original fluid at Kizildere is estimated under the assumption of calcite saturation at 210°C and total pressure of 74 bar at 900 m. CO$_2$ exsolution starts at about –600 m, where 53.6 bar prevail of which 39 bar account for CO$_2$. Under these assumptions total dissolved Ca is estimated to be 0.123 mmol/kg at pH of 6.1. From -600 m to surface steam is produced, by which the conservative elements are concentrated in the liquid and the initial CO$_2$:H$_2$O vol. ratio of vapour of 2.7:1 drops to 1:14 under well head conditions. The concentration factor (CF) of conservative elements due to evaporation in the bore hole is derived from enthalpy changes of the vapour (Keenan et al., 1969). The changes of enthalpies of the liquid at temperatures T1 and T2, $\Delta H_{T1}$ and $\Delta H_{T2}$ and of the average change of enthalpy of evaporation between different temperatures T1 and T2, $\bar{\Delta H}_{\text{evap}}$, are used to estimate the fraction of evaporating water $\alpha_{T1}^{T2}$ neglecting heat loss to the surroundings (eq. (9) and eq. (10)).
\[ \alpha_{T_1}^{T_2} = \frac{\Delta H_{T_2} - \Delta H_{T_1}}{\Delta T_{\text{evap.}}} \]  

(9)

\[ app \, CF_{T_1}^{T_2} = \frac{1}{(1 - \alpha_{T_1}^{T_2})} \]  

(10)

During ascent from depth to surface, paralleled by cooling from 210 to 190 °C, about 5% of the primary liquid evaporates which corresponds to an enrichment of conservative elements in the liquid by a factor of 1.05. With a minimum of dissolved Ca of 0.024 mg/kg in well head fluids (Table 3), 0.123-0.024/1.05= 0.10 mmol/kg-fluid are precipitated in the borehole, which is equal to 10 mg carbonate-scale/kg-fluid. This amounts to an average of about 16 tons per 11 month, which is the normal production period of each well at Kizildere.

The saturation indexes of minerals (SI) indicate that the well head fluids are mostly supersaturated with respect to calcite. Their cooled equivalents, however, are strongly undersaturated with respect to calcite at 50°C and 1 bar. Particularly, the condensates of vapours are strongly undersaturated with respect to carbonates at sampling temperatures.

### 7.2.5 Apparent distribution factor of REY between HTF and source rock

The analysed Palaeozoic and Mesozoic rocks of W Anatolia and Tuscany (Table 5) show REY patterns with rather similar trends and negative Eu anomalies (Fig. 17). The ratio of REY/Ca ratio in HTF and REY/Ca ratio of the corresponding source rocks yield apparent distribution factors, \( app \, K_{HF}^{source-rock} \) (Fig. 17). In the long-time producing geothermal system of Larderello-Travale and Kizildere the apparent distribution factors are about 0.1 without depicting any anomalous behaviour of Eu or Y. Those determined for Monte Amiata are 1 – 2 orders less with strong Eu and Y anomalies. The reasons for the considerable spread of \( app \, K_{source-rock} \) is not known yet.

\[ app \, K_{HF}^{source-rock} = \left( \frac{\text{REY/Ca}}{\text{Ca/REY}} \right)_{HTF} \left( \frac{\text{REY/Ca}}{\text{Ca/REY}} \right)_{source-rock} \]  

(11)

Using the derived distribution factors (eq.11) and \([Ca]_{\text{original}} = 0.024 \text{ mmol/kg}\) (the lowest Ca concentration determined in Fig. 15), REY are back-calculated according to eq(12). The factor 1.05 refers to evaporation of water during ascent.

\[ \frac{[\text{REY}_{\text{original}}]}{[\text{Ca}_{\text{original}}]} \frac{1}{1.05} - \frac{[\text{REY}_{\text{SP1}}]}{[\text{Ca}_{\text{SP1}}]} \]  

\[ app \, K_{\text{fluid}}^{scale} = \frac{[\text{REY}_{\text{SP1}}]}{[\text{Ca}_{\text{SP1}}]} \]  

(12)
The REY composition of the Kizildere fluid under source rock condition yields higher REY abundance by a factor of 2 than in the well head water of Kizildere, whereas the Ca contents are higher by a factor of 5 under the same conditions.

At Monte Amiata, the fluids were condensed under pressure. Thus, REY are contained in the resulting liquid. The REY content of the vapour at 30°C is negligible. At Larderello-Travale only steam is produced. The REY of the initial fluid are back-calculated by using the vapour/liquid distribution coefficients from Fig. 18.

Table 5: Rare earth elements yttrium and calcium abundance in back-calculated liquids under source conditions.

<table>
<thead>
<tr>
<th>Field</th>
<th>Kizildere</th>
<th>Monte Amiata</th>
<th>Larderello-Travale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Locality/wells</td>
<td>Kizildere</td>
<td>Piancastagnio</td>
<td>Piancastagnio</td>
</tr>
<tr>
<td>Source rock</td>
<td>Mica schist/marble</td>
<td>Limestone/ evaporites</td>
<td>Phyllite</td>
</tr>
<tr>
<td>Ca mg/L</td>
<td>0.12</td>
<td>19.2</td>
<td>3.31</td>
</tr>
<tr>
<td>Y pmol/L</td>
<td>7.07</td>
<td>17.9</td>
<td>51.7</td>
</tr>
<tr>
<td>La</td>
<td>3.60</td>
<td>9.25</td>
<td>9.16</td>
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<tr>
<td>Ce</td>
<td>7.88</td>
<td>27.8</td>
<td>16.6</td>
</tr>
<tr>
<td>Pr</td>
<td>0.79</td>
<td>2.60</td>
<td>2.09</td>
</tr>
<tr>
<td>Nd</td>
<td>2.35</td>
<td>7.81</td>
<td>7.68</td>
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<tr>
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</tr>
<tr>
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<td>1.71</td>
</tr>
<tr>
<td>Gd</td>
<td>0.40</td>
<td>1.21</td>
<td>2.37</td>
</tr>
<tr>
<td>Tb</td>
<td>0.08</td>
<td>0.18</td>
<td>0.39</td>
</tr>
<tr>
<td>Dy</td>
<td>0.50</td>
<td>1.01</td>
<td>2.53</td>
</tr>
<tr>
<td>Ho</td>
<td>0.10</td>
<td>0.19</td>
<td>0.52</td>
</tr>
<tr>
<td>Er</td>
<td>0.28</td>
<td>0.53</td>
<td>1.58</td>
</tr>
<tr>
<td>Yb</td>
<td>0.31</td>
<td>0.50</td>
<td>1.68</td>
</tr>
<tr>
<td>Lu</td>
<td>0.07</td>
<td>0.26</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 18: Averaged apparent partition coefficient $^{app}KD_{HEF}^{rock}$ for the geothermal systems of Monte Amiata, Larderello-Travale and Kizildere.
8. Conclusions

Rare earth elements (REE) and Y abundances in aqueous, low- to high-temperature fluids cover 6 orders of magnitudes. REY abundance in the exploited CO₂ rich geothermal liquids with pH values of about 6.5 (50°C) and well head temperatures exceeding 190°C are below 1 pmol/kg, excepting La, Ce and Y. The REY abundances in these waters originate from metamorphic rock sequences and are about two orders of magnitude lower than those reported for Icelandic circum-neutral (Aggarwal et al. 1996) water from basalts, or acidic waters from rhyolites of the Yellowstone National Park (Lewis et al. 1998) and Japanese crater lakes (Kikawada et al. 1993). REY are omnipresent in minerals and fluids. Considerable fractions of REY are hosted by accessory minerals in rocks and sediments. Some of them are leachable especially by CO₂ rich waters. Accessory minerals are typical for each type of sediment REY patterns of groundwaters differ from those of the aquifer rocks. REY patterns of groundwaters are characteristic for the types of rocks at least on a regional scale. Anomalous behaviour of Ce, Eu, and Y are indicative for water-rock interaction processes. Anomalies inherited from source rocks can be distinguished from those acquired during fluid migration. The absence of acquired anomalies indicate steady state conditions. REY patterns yield information on the source of geothermal fluids, temperature range (Eu), and redox values (Ce), intensity of adsorption during migration (Y). The strong relation to Ca couples the distribution of Ca and REY in all kinds of processes such as fluid rock interaction, and scale formation. Only in vapours these elements are decoupled. It has been found:

- Evaporation and depressurisation during ascent is accompanied by little REY fractionation enforced by coprecipitation of REY with carbonates.
- The fluids - scale formation distribution coefficients of REY \( K_d^{scale} \) or \( K_d^{fluid} \) at about 190°C are less than 1, but vary within 1 order of magnitude.
- The REE abundance in the high-temperature fluid ranges from 0.01 to about 10 pmol/kg. The REY/Ca ratios of the HTF related to the corresponding ratios of the source rocks yield distribution factors ranging from 0.01 to 0.1, independent on source rock composition. REY are largely retained by alteration minerals in rocks and sorption on mineral surfaces.
- The partition factors defined by the abundance ratio in vapour and liquid are in the range of 0.05 to 0.4. These factors are higher than those of earth alkaline and alkaline elements.

Knowing REY partition coefficients with scales and Ca contents of the original fluid, it is possible to back-calculate the REY abundance under bottom hole conditions. The variability of Ca concentration in the well head water is dependent on the state of equilibration with carbonate precipitation. Under optimal conditions four-fifth of the primary Ca concentration in the original fluid is precipitated in boreholes at Kizildere. Together with calcite REY are coprecipitated. Thus, the REY abundance in the original fluids is higher than determined in the well head fluids.
8. References


