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REE Systematics of Reservoir Rocks in Kizildere Geothermal Field, Turkey

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ABSTRACT

The Kizildere Geothermal Field is located on the easternmost of the Büyük Menderes Graben, Western Turkey. This graben and several other grabens, which have been developed almost parallel to each other, are located at the easternmost of the Aegean Extensional System. The field contains several liquid dominated reservoirs hosted in fractured sedimentary and metamorphic rocks; this study focused on the reservoir in mica-schist units with secondary permeability.

The REE mobility has been investigated taking into account the mineralogy and geochemical composition of the reservoir rock in this high-enthalpy geothermal field. Drill cutting samples were collected at different depths in a geothermal well and the mineralogy was constrained using petrography and XRD analysis. REE compositions of the samples were determined as well, using the ICP-OES technique. These data are evaluated along with the well-log data to assess the relationship between mineralogy and REE composition in this well.

Our data suggest that the samples can be divided into two groups based on alteration mineralogy, and well-log data such as mud loss and temperature changes detected during drilling: 1. hydrothermally altered rocks in fault zones, and 2. unaltered rocks away from the fault zones. According to the XRD analysis, the major constituents of the unaltered samples are quartz, albite, muscovite, and chlorite. Illite, kaolinite, dickite, calcite, dolomite, and ankerite occur with these minerals at the fault zones.

PAAS-normalized REE results indicate that samples from the fault zones have similar REE patterns to the unaltered units. In terms of particular ratios like $(La/Lu)_n$, $(La/Sm)_n$, and $(Gd/Lu)_n$ the two groups of samples cannot be distinguished using a Mann-Whitney U test results. However, ∑REE differs between the two groups statistically. The altered samples that contain secondary minerals have negative Ce anomalies and lower normalization values. The difference of ∑REE between the two groups of samples is in the ∑LREE rather than the ∑HREE.

1. INTRODUCTION

1.1 Significance and Use of REE in Geothermal Systems

The Rare earth elements (REE) range from La through Lu on the periodic table. The first six elements from La to Sm are termed the light REEs (LREE) and the others (Eu to Lu) are the heavy REEs (HREE). The REE elements occur at low concentrations in rocks but changes in their abundance can elucidate processes such as water-rock interaction in a geothermal system (Michard and Albarède, 1986, Möller, 2002, Möller et al., 2008, Fowler et al., 2019). They occur in the lattice of many rock-forming minerals but also can be found absorbed on mineral surfaces at low temperatures (Möller et al., 2003, Möller et al., 2008) In the active hydrothermal systems such as non-magmatic, convection-dominated, geothermal systems, meteoric water is the agent of REE mobility. Meteoric water acquires REE as it circulates in the geothermal system and several parameters that control this phenomenon (Hopf, 1993, Haas et al., 1995).

Hopf (1993) indicates that some of the REE released by the breakdown of primary phases during alteration are transported away in the fluid. The similarity of REE patterns resulting from alteration by alkaline and acid fluids suggests that the shape of the REE trends is controlled principally by fluid/rock ratios and by mineralogy. The REE is retained in rocks with diverse alteration mineralogy in the system. There are studies that demonstrated that fractionation related REE mobility during alteration (Taylor and Fryer, 1980, Taylor, 1982, Terakado and Fujitani, 1998, Takahashi et al., 2004, Pirajno, 2012). The study of Taylor and Fryer (1980) indicates that REE distribution in unaltered and altered rocks can be taken as evidence of changing fluid conditions from dominantly magmatic to dominantly meteoric.

It can be mentioned several parameters that control the alteration process responsible for REE mobility in the active hydrothermal systems. These include the solubility of the REE hosting minerals, nature of the complexation of the REE on mineral surfaces, the temperature and water-rock ratios, etc. The REE may then be precipitated in other parts of the system (Browne, 1978). Therefore, the aim of this study is to determine the behavior of the REE mobility in the reservoir in the Kizildere Geothermal Field.

1.2 Study Area

The Kizildere Geothermal Field is a rare example of a non-magmatic, convection-dominated geothermal play in the world (Moeck, 2014). The field is developed in the Menderes metamorphic core complex which was uplifted by the subduction of the Eastern Mediterranean lithosphere under the Anatolian plate in this region during Miocene (Şengör and Yilmaz, 1981). As a result, Büyük Menderes Graben, and several other grabens which have been developed almost parallel to each other, formed in the easternmost part of the Aegean extensional regime (Şengör and Yilmaz, 1981, Mercier et al., 1989, Görür et al., 1995).

The stratigraphy of the field was first presented by Şimşek (1985) The basement metamorphic rocks are the Paleozoic aged metamorphic rocks of the Menderes Massif. This is composed of augen gneisses, schists, quartzites, mica schists, and marbles (Figure 1). These units are overlain by the Lower Pliocene Kızılburun Formation (Tk) which consists of conglomerates and sandstones, the Sazak Formation (Ts) comprising intercalated limestones and marls, the Kolonkaya Formation (Tko) made up of marls, sandstones and siltstones and the Tosunlar Formation (Tt) which has poorly consolidated conglomerates, sandstones and mudstones with fossiliferous clays. Quaternary alluvium, terrace, and travertines overlie these rock sequences (Figure 1).

The Kizildere Geothermal field has three distinct reservoirs. The uppermost reservoir lied within the limestones of Sazak Formation and is referred to as the "shallow reservoir". A second reservoir is hosted in marble-quartzite-schist intercalations of the Paleozoic metamorphic rocks. The third, "deep reservoir" is hosted in gneisses and quartzites underlain by schists (Figure 1)(Simsek et al., 2005).

The Kizildere Geothermal field is not associated with the magmatic activity. In this system, fault-controlled convection occurs along the normal faults of the Büyük Menderes Graben. The main graben fault (which is Gökdere Fault for this field) and its conjugated normal fault sets control the flow of meteoric water to the deep reservoir. Here, a complex system of E-W striking, south-dipping faults with a maximum ~1000m displacement on the border of the graben intersects another ENE striking sub-vertical fault system allows fluid and heat transfer in the reservoir rocks (Şimşek, 1985, Simsek et al., 2005, Faulds et al., 2009).

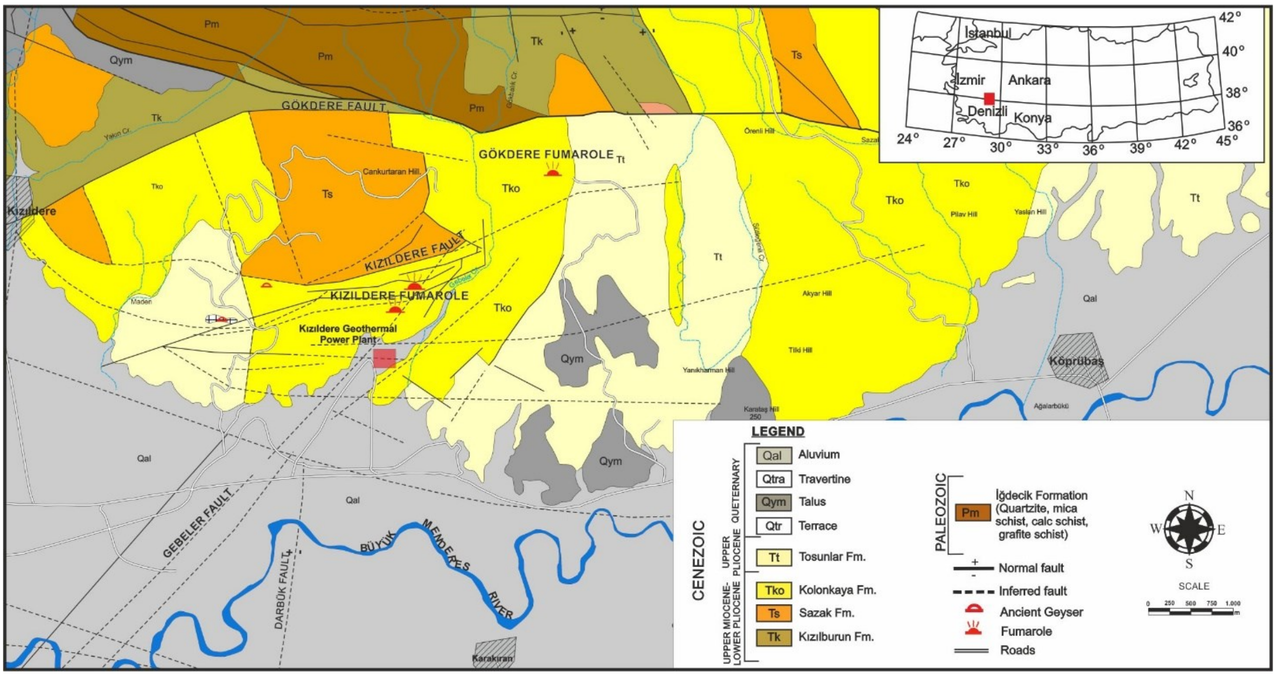

Figure 1. Simplified geologic map of the Kizildere Geothermal Field. (modified after Şimşek, 2014)

2. METHODS

2.1 Whole-rock samples of Reservoir Rocks

Samples of drill cuttings of the reservoir units from geothermal well 44 from the field were taken. The well was drilled to a total depth of 2703 m, with a mud rotary system with diamond carbide and diamond tri-cone drill-tips. The cuttings obtained by this method had varying grain sizes, from fine to coarse. These cuttings were logged and approximately 0,5 kg of rock fragments were collected every 4 m and then powdered for analyses.

XRD analyses made by the XRD device used in this study is a GNR APD-2000 in Istanbul University-Cerrahpaşa. Diffractograms obtained with Cu Ka radiation, Ni filter, 40 kV voltage, 30 mA current $2\theta = 1^{o}$ / min goniometer speed 1 cm / min intensity. The diffractograms were then evaluated by pairing JCPDS cards with Pananalytical High Score Plus software to define the minerals.

Samples were analyzed to determine REE concentrations at GFZ Potsdam Research. Samples were prepared for REE analyses using the method of Zuleger and Erzinger (1988). This method has been developed to concentrate the REE and Y elements in the sample and avoid overlapping the other element peaks and REE and Y peaks during measurement, resulting in misinterpretation of the results.

2.2 Statistical Comparison Method

To statistically assess the data, IBM SPSS Statistics software was used. In the sciences and social sciences, several methods are available to test whether two independent groups are significantly different from each other. The primary purpose of these tests is to determine statistically whether the central tendencies (mean or median) of the two groups differ from each other based on samples of the two groups. The most common methods are the T-test, ANOVA (F-test), and Mann-Whitney U test. The T-test and ANOVA tests are parametric; the Mann Whitney U test is a nonparametric test. Parametric tests are applied to samples where data is distributed normally or lognormal. If the distribution of the variables is not normal in the data set, nonparametric tests should be used.

The Mann-Whitney U test is generally considered as the nonparametric equivalent of the independent sample T-test. However, the Mann-Whitney U test is used with non-parametric data (typically sequential data); the independent sample T-test is used for data that satisfies the assumptions of parametric distributions (normal distribution). Although parametric tests are more widely used, the

Mann-Whitney U test has many convenient uses. When sequential data are used, it is used to reveal whether there are significant differences in the data that are deviating from the distribution or in two independent groups (MacFarland and Yates, 2016).

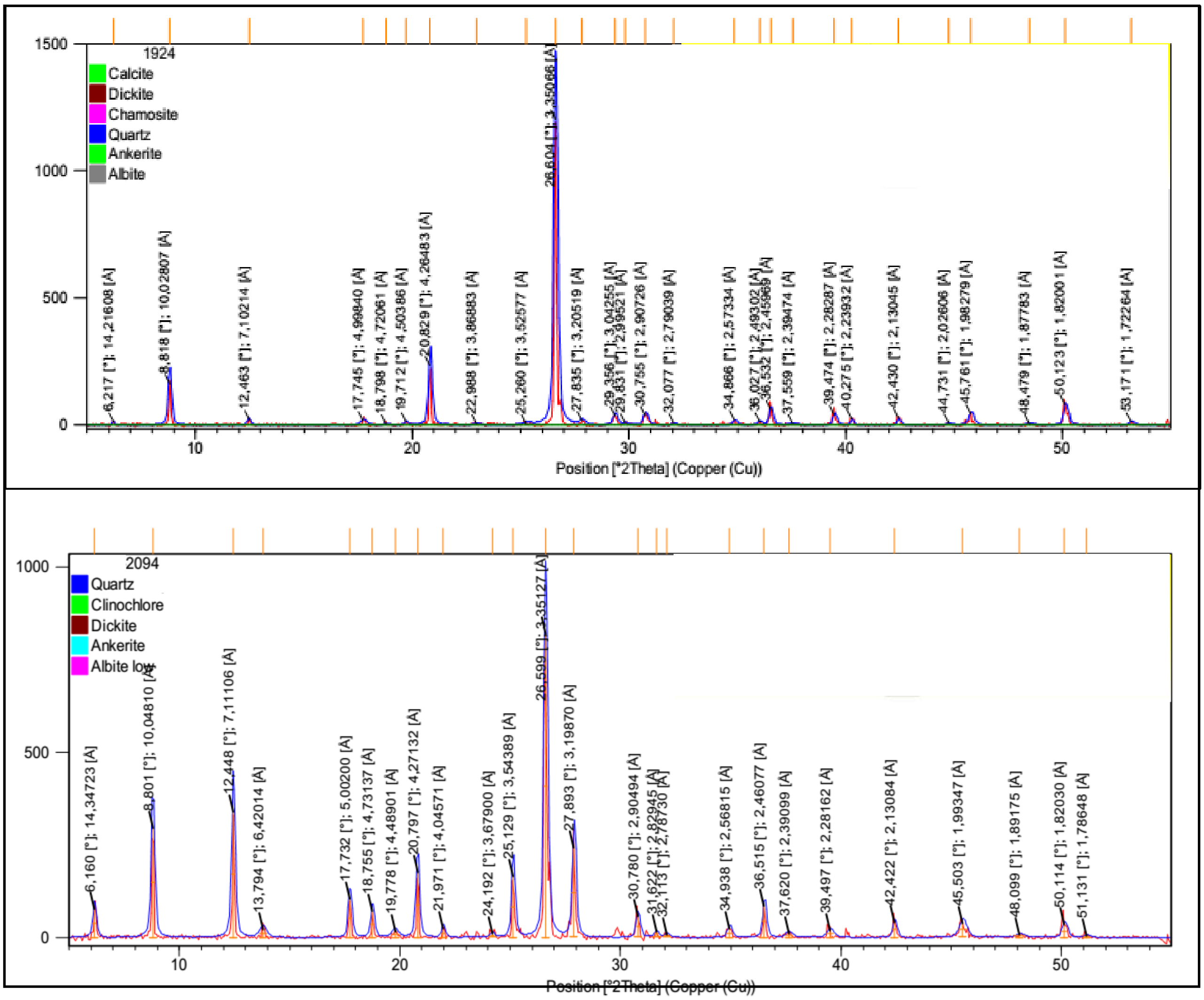

Figure 2. Exemplary XRD pattern of hydrothermally altered rocks in fault zones of the well (1924th and 2096th meters). The values of the picks indicate position [°] and d-spacing [Å], respectively. I (100%) values for minerals in the database are Quartz: 26,995; 3,30029; Clinochlore: 12,473; 7,1194; Albite: 27,894; 3,19600; Dickite: 8,763; 10,08290; Chamosite: 12,504; 7,07363; Ankerite: 30,742; 2,90600; Calcite: 29,369; 3,03867

3. RESULTS AND DISCUSSION

3.1 Mineralogy of the Drill Cuttings

We analyzed 40 samples by XRD collected every 4 meters in the well. These samples represent 180 meters of the reservoir. This interval starts from 1924th meter and ends up at 2104th meter of the well. In order to determine this, we interpreted sub-surface structural maps and cross-sections of the reservoir units. The main fault zone has been determined according to seismic cross-sections. Samples have been collected this interval contains the main fault zone.

Determination of the minerals out of the XRD pattern has been done using X-pert High Score Plus software. The software identifies minerals fit to the spectra. However, because of the reservoir rocks of the Kizildere Geothermal field consist of schists, quartzites, and calc-schists (Şimşek, 1985), the minerals that impossible to occur in metamorphic environments were eliminated, and suitable minerals found from ICDD database to match with the picks of the pattern.

The minerals obtained in all 40 samples can be listed as follows: Quartz, muscovite, albite, clinochlore, anorthite, phlogopite, rutile, annite, graphite, calcite, dolomite, kaolin, dickite, ankerite, vermiculite, faujasite, and lucacite. The XRD patterns of the samples from 1024th, 2056th, 2084th and 2094th meters are given in Figures 2 and 3. These exemplary patterns are shown common minerals such as quartz, muscovite albite, and clinochlore. The others additionally have phlogopite, rutile, annite, and graphite. These minerals are rock-forming minerals of schists and determined almost all samples. When the XRD patterns have only these rock-forming minerals these samples are grouped as unaltered rocks. Twenty-four samples in the sample set have been included in this group.

On the other hand, the remaining sixteen samples represent hydrothermally altered rocks from the fault zones according to the results of XRD analysis. These low-grade green-schist facies mineral paragenesis has been accompanied by illite, kaolinite, dickite, calcite, dolomite, and ankerite in fault zone samples (Figure 3 2). These minerals can occur in low temperature hydrothermal and geothermal systems (Kristmannsdóttir, Browne, 1978, Reyes, 1990, Fulignati et al., 1999, Verma et al., 2005, Marks et al., 2010)

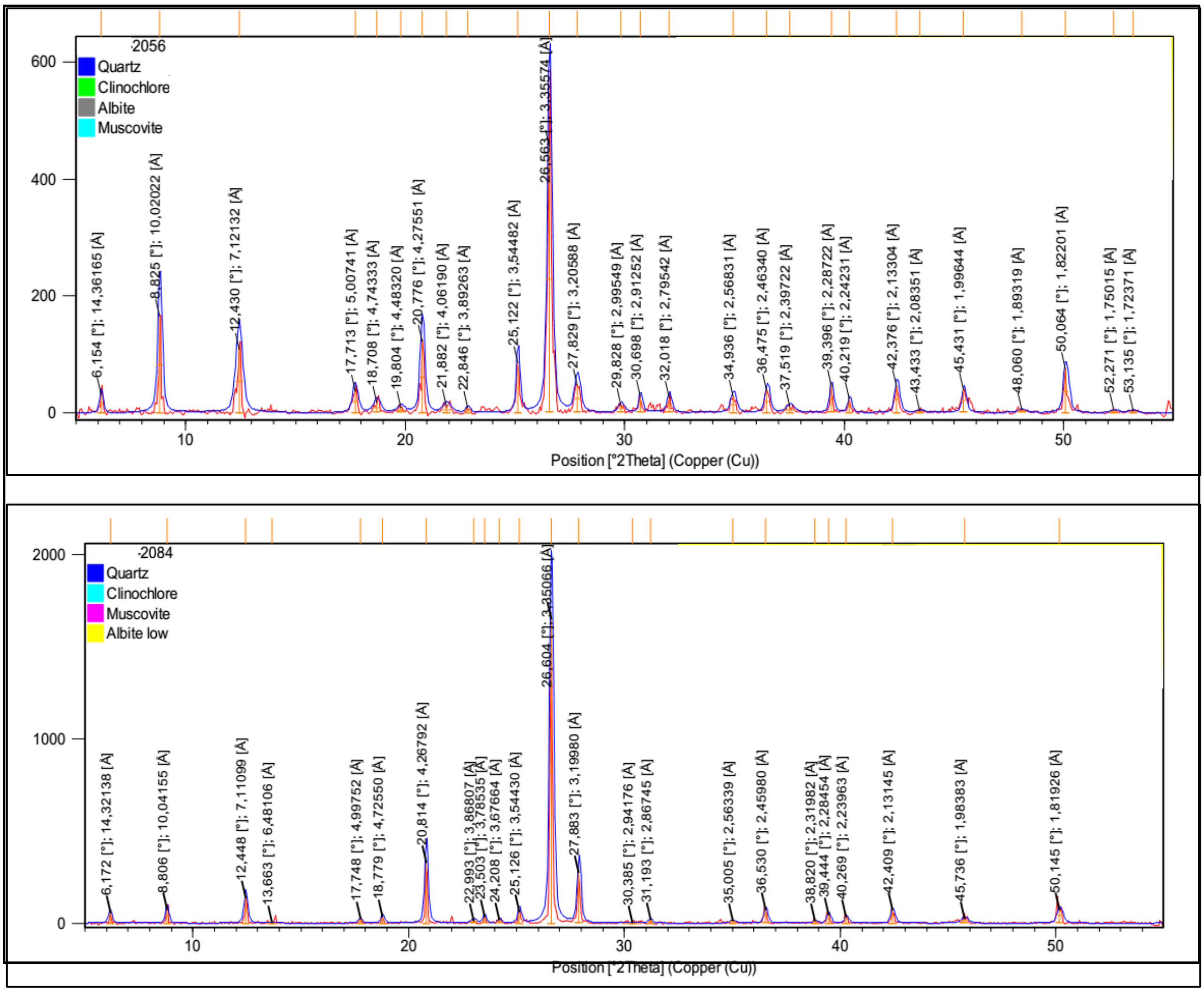

Figure 3. Exemplary XRD pattern of unaltered rocks away from the fault zones of the well (1924th and 2096th meters). The values of the picks indicate position [º] and d-spacing [Å], respectively. I (100%) values for minerals in the database are Quartz: 26,995; 3,30029; Clinochlore: 12,473; 7,1194; Albite: 27,894; 3,19600; Muscovite: 34,998; 2,56175

3.2 REE Concentration of the Cuttings

Twenty-six samples of unaltered rocks and 16 samples of fault rocks were analyzed for REE concentrations. The data have been normalized to PAAS (Post Archaen Australian Shale) because of the protoliths of the reservoir rock. In Figure 4, the unaltered rocks are shown as a grey shaded area, but the individual analyses of the 16 fault rock samples have been plotted.

The PAAS-normalized REE results indicate that the fault zone samples have similar REE patterns to the unaltered rocks. The altered samples with secondary minerals generally have negative Ce anomalies and several samples have lower normalization values. This may suggest that these can be indicated REE addition to the system with hydrothermal fluids (Figure 4Figure 4).

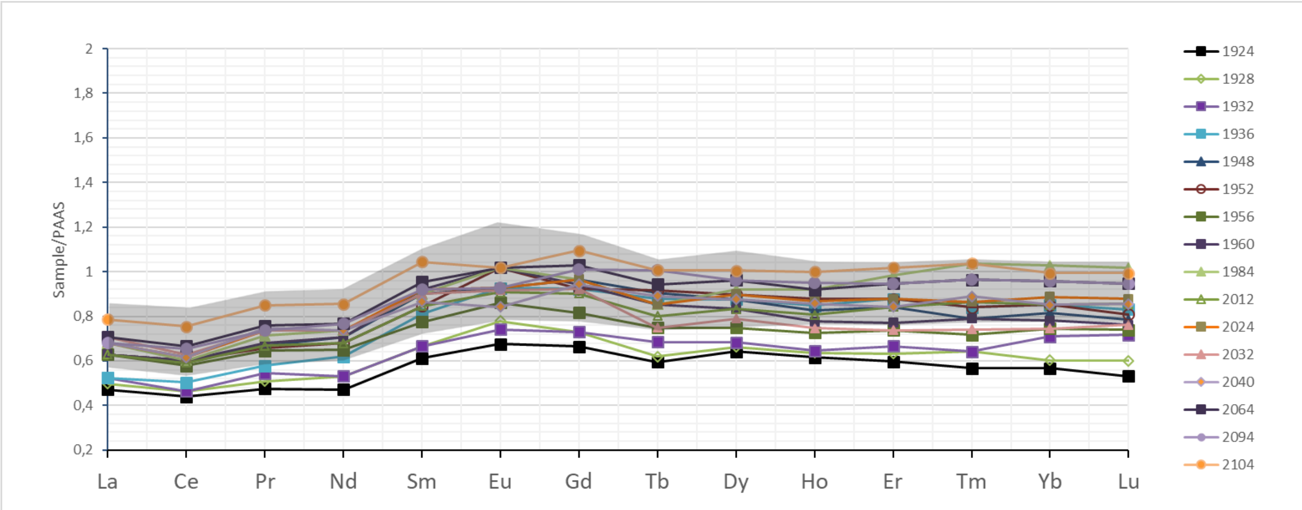

Figure 4. REE patterns of drill cutting samples. The shaded area represents the field of the samples determined as unaltered samples away from the fault zones. The other 16 samples of hydrothermally altered fault zone plotted separately for comparison.

Some ratios such as $(La/Lu)_n$, $(La/Sm)_n$, $(Gd/Lu)_n$ have been used to help interpretation of the alteration process. $(La/Lu)_n$ can be used to assess the fractionation of LREE relative to HREE. $(La/Sm)_n$, and $(Gd/Lu)_n$ assess any fractionation within the LREE or HREE respectively (Hopf, 1993, Henderson, 2013). When all the ratios are plotted with depth, there is a difference between the altered and unaltered rock samples. Specifically, the LREE seem less resistant to the hydrothermal processes in the ∑REE. The significant amount of the deviation from the mean relative to the other two ratios, in general, (Figure 5).

3.3 Statistical Comparison

After plotting these samples by depth, it was necessary to see if the differences between the sample groups were meaningful or not. Verma et al. (2005) have been implemented this comparison method and taken satisfactory results. It has been used the statistical test called Mann Withney-U test for the same purpose in this study.

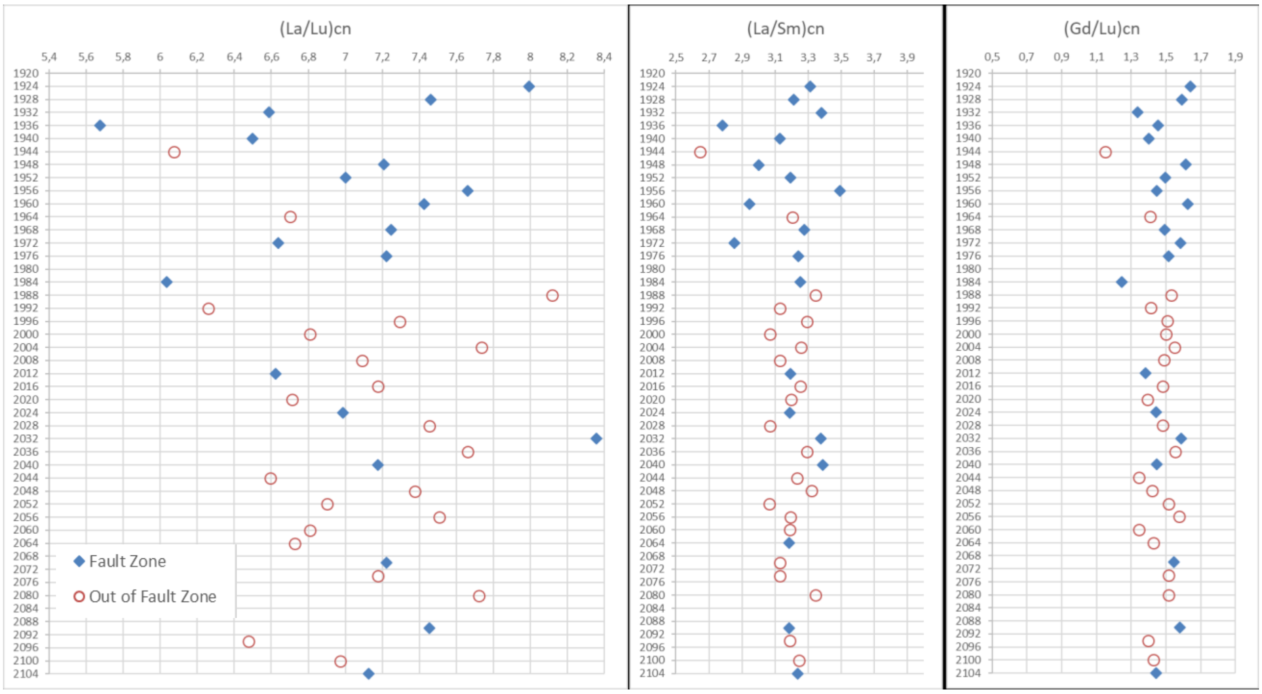

Figure 5. REE ratios to interpret the fractionation during hydrothermal processes. Graphs have been plotted downhole by depth (in meters).

According to the results of the non-parametric test, some variables i.e. ∑REE, ∑LREE, and Ce anomalies have lower significance (p) value than 0,05. Z scores are also lower than -1,96 for these three parameters.This means we need to reject null hypothesis. It means that these three parameters have meaningful differences between the two groups. It can be said that the difference of ∑LREE between two groups caused the difference rather than the difference of ∑HREE (**Error! Not a valid bookmark self-reference.**).

Table 1. Comparison of some REE ratios of between hydrothermally altered rock samples and unaltered rock samples. Statistical parameters indicated the scores of the Mann-Whitney U test (p<0,05). (h_1 is valid for parameters in grey lines)

	Mann-Whitney U	Wilcoxon W	Z	p
∑REE	127,000	263,000	-2,098	**,036**
∑LREE	125,000	261,000	-2,150	**,032**
∑HREE	158,000	294,000	-1,295	**,195**
$(La/Lu)_n$	190,500	326,500	-,453	**,650**
$(La/Sm)_n$	175,000	526,000	-,856	**,392**
$(Gd/Lu)_n$	205,500	341,500	-,065	**,948**
[Ce]/[Ce*]	117,500	253,500	-2,345	**,019**
[Eu]/[Eu*]	170,000	521,000	-,984	**,325**

4. CONCLUDING REMARK

The geothermal fluids circulate in fractures in these units formed during tectonic events. Meteoric water comes down to the reservoir through these fractured zones (mainly normal faults) and during its travel, the temperature of the water has got higher in the reservoir. This so, some altered zones form trough the fluid pathways. Revealing the mineralogy of the drill cuttings was essential for this study to determine these fluid pathways. Hydrothermal alteration related occurrences would point out the zones that hot fluids travel in the system.

According to XRD analysis, the major constituents of the unaltered samples are quartz, muscovite, albite, clinochlore, anorthite, phlogopite, rutile, annite, graphite. These results are consistent considering the stratigraphy of the geothermal field. In the hydrothermally altered zones minerals mention before accompanies by calcite, dolomite, kaolin, dickite, ankerite, vermiculite, faujasite and lucacite. Our data suggest that the samples can be divided into two groups, one of the altered rocks caused hydrothermal circulation in fault zones and a second group of unaltered rocks from outside of the fault zones. This grouping is based on alteration mineralogy, and well-log data such as mud loss and temperature changes detected during drilling.

The results of our study reveal that hydrothermal processes active are effective in reservoir rock in the Kızıldere Geothermal Field. Mineralogical changes on parent rock can be observed by analitical methods. The changes in the∑REE concentration of the reservoir rock depend on the mineralogy. Results of the Mann-Whitney U test indicates these differences statistically.

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