ORIGIN OF HIGH SULFATE CONTENTS IN THE THERMAL WATERS OF KIZILDERE AND ENVIRONS, WESTERN ANATOLIA, TURKEY

Nevzat Özgür
Süleyman Demirel Üniversitesi, Research and Application Center for Geothermal Energy, Groundwater and Mineral Resources, 32260 Isparta, Turkey
and
Wolfgang Graf, Willibald Stichler, and Manfred Wolf
GSF-Institute of Hydrology, Ingolstädter Landstraße 1, D-85764 Neuherberg, Germany

ABSTRACT

In thermal waters of Kızıldere and environs, there are sulfate concentrations of up to 1.665 mg/l which differ from other thermal waters in the Menderes Massif extremely. The source of sulfur, which encounters a transformation to sulfate ions by disproportionation and is found in thermal waters of Kızıldere and environs, can be attributed to a magmatic input due to isotope ratios of $\delta^{34}S$ in sulfate and sulfide precipitations of thermal waters. The magmatic origin of sulfur might be corroborated by the isotope ratios of $\delta^{13}C$, $\delta^{11}B$, and $^{3}He/^{4}He$ of the thermal waters in the investigated area. The gypsum occurrences and diagenetic pyrite ore minerals in Pliocene sedimentary rocks form a second source of high sulfate contents in thermal waters of Kızıldere and its environs.

INTRODUCTION

The thermal waters of Kızıldere and environs in the rift zone of the Büyük Menderes are distinguished by their extremely high sulfate contents of up to 1.665 mg/l (Özgür, 1998) and differ from the others in the Menderes Massif, e.g. Salavatlı, Germencik, Bayındır and Salihli (Özgür, 1998), thereby. The thermal field of Kızıldere is located in the eastern part of the continental rift zone of the Büyük Menderes and surrounded by a multitude of other hydrogeochemical different hot springs with a temperature range from 35 °C to 92 °C (Fig. 1). Since 1984, a 17,5 MW geothermal power plant is existing in Kızıldere and operated by Turkish state Electricity Company. The geothermal energy produced from nine wells is forwarded to general national electricity network. Moreover, CO_2 in steam phase constituting 10 percent of total production is dealt separately and processed to dry ice in plant area.

The aim of this paper is to elucidate the origin of high sulfate contents in thermal waters of Kızıldere and environs in consideration of geochemistry and isotope geochemistry of $\delta^{34}S$ and $\delta^{18}O$.

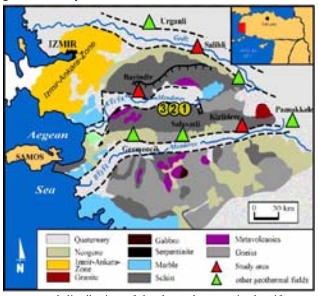

Fig. 1: Location map and distribution of the thermal waters in the rift zone of the Büyük Menderes.

GEOLOGIC SETTING

The Thermal field of Kızıldere consist of Precambrian to Cambrian metamorphic and Pliocene sedimentary rocks (Özgür, 2001; Şimsek, 1985; Fig. 2). The metamorphic rocks are gneiss, mica schists and Igdecik formation consisting of mica schists, quartzites, and marbles. The Pliocene sedimentary rocks discordantly overlie the metamorphic basement and are continental lacustrine. The sedimentary rocks can be subdivided as (i) the Kızılburun formation, (ii) the Sazak formation, (iii) the Kolonkaya formation, and (iv) the Tosunlar formation stratigraphically (Fig. 2).

The continental rift zone of the Büyük Menderes shows E-W directions generally and was generated in Middle Miocene. In respect of tectonics, the thermal waters in Kızıldere and environs are linked to faults in NW-SE or NE-SE directions, which are diagonal to main faults in E-W. These additional faults were presumably generated by a compressional stress which leads to deformation of horst between two extension rift zones. In connection with thermal waters, the rift zone of the Büyük Menderes is distinguished by the existence of young volcanic rocks in Denizli, Söke and Selcuk. The volcanic rocks in Denizli are of Late Pliocene age and those in Kula are ranging in age from 7,5 Ma to 18.000 up to 20.000a (Ercan et al., 1992). These volcanics can be considered as heat source for the heating of meteoric fluids in the investigated area.

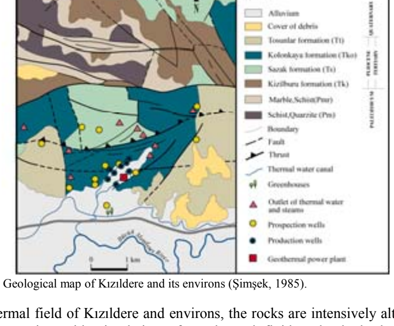

Fig. 2: Geological map of Kızıldere and its environs (Şimşek, 1985).

In thermal field of Kızıldere and environs, the rocks are intensively altered by interaction with circulation of geothermal fluids. The hydrothermal alteration is noticeable at the surface which is distinguished by phyllic, argillic, silicic alteration ± hematitization, and carbonatization alteration zones (Özgür, 1998). The carbonatization takes place in calcareous sedimentary rocks and can be observed in the fault zones of the thermal field of Kızıldere preferentially. By release of Ca^{2+}, SO_4^{2-} and HCO_3^- from thermal waters, $CaSO_4.2H_2O$ and $CaCO_3$ form at surface and in joints. Therefore, the Pliocene sediments contain layers with gypsum crystals in diameter of several dm which can be considered as source of high sulfate contents in the thermal waters of Kızıldere and environs. In the thermal field of Kızıldere and its environs, Precambrian to Cambrian metamorphic and Pliocene sedimentary rocks are distinguished by the enrichment patterns of Hg, Sb, As, Tl, Ag, and Au and the depletion patterns of alkaline and earth-alkaline elements in connection with degree of hydrothermal alteration geochemically (Özgür, 2001, 2002).

HYDROGEOLOGY AND HYDROGEOCHEMISTRY

The groundwater conditions in drainage area of the thermal field of Kızıldere can be reconstructed by morphological features and analogy conclusions. Groundwater flow takes place in the Buldan horst in the north of the rift zone of the Büyük Menderes to south; the thermal waters reservoirs are supplied directly thereby. The distance from watershed to the thermal field amounts 10 km approximately. The drainage area takes up an area of 100 to 150 km^2 consequently.

In the thermal field of Kızıldere, the Sazak formation consisting of limestones, marls and siltstones forms the first shallow reservoir with a temperature of 198 °C at a depth of 400 m (Özgür, 2001). The Igdecik formation composed of quartzites, mica schists and marbles is second deep reservoir at a depth of 1000 to 1242 m and a temperature up to 212 °C. Hydrogeochemically, the thermal waters of Kızıldere, especially 8 production wells, are of $Na\text{-}HCO_3\text{-}SO_4$ type exchange water whereas the waters from the environs can be considered as $Ca\text{-}Na\text{-}HCO_3\text{-}SO_4$ type indicating a mixing of a thermal sodium bicarbonate component, cold calcium sulfate component and a cold calcium bicarbonate component in different proportions (Özgür, 2001).

As trace elements, e.g. F and B, heavy metals of As and Sb are found in high concentrations (Özgür, 2002) and show a close correlation with one another depending upon increasing temperature conditions. The origin of fluorine and boron is related to a magmatic activity whereas the source of As and Sb can be assigned to the metamorphic rocks established by leaching tests (Özgür, 1998). The SO_4^{2-} concentrations range from 613 to 1.111 mg/l in thermal waters of Kızıldere and from 334 to 1.665 mg/l in groundwater-thermal water systems whereas the groundwater from Buldan shows a SO_4^{2-} value of 70 mg/l (Özgür, 1998).

MATERIAL AND METHODS

In order to elucidate the origin of the high sulfate concentrations in the thermal waters of Kızıldere and its environs, 5 sulfate and 1 sulfide precipitate from the investigated area were prepared for $\delta^{34}S$ and $\delta^{18}O$ analyses (Özgür, 1998). For comparison, sulfate precipitations of groundwaters and thermal waters of Bayindir, Salihli, and Seferihisar have been used. Moreover, a gypsum sample in Pliocene sedimentary rocks was analyzed for $\delta^{34}S$ and $\delta^{18}O$. A multitude of $\delta^{34}S$ analyses of sulfide ore samples from epithermal mercury, antimony, and arsenopyrite-gold deposits in the rift zone of the Kücük Menderes was available (Özgür, 1998).

After geochemical analyses of groundwaters and thermal waters and calculation of carbonate and sulfate contents, the fluid samples were treated with $BaCl_2.2H_2O$ to precipitate carbonate and sulfate concentrations by increase of pH value up to 11 using carbonate free NaOH during a field campaign. Gypsum sample and the sulfate and sulfide precipitates were analyzed by mass spectrometry at GSF-Institute of Hydrology, Neuherberg, Germany.

ISOTOPE GEOCHEMISTRY

The $\delta^{34}S$ isotope ratios range from 19,1 to 19,4 ± 0,3 (‰) CDT in thermal waters of Kızıldere and from 17,2 to 17,98 ± 0,3 (‰) CDT in thermal waters of environs of Kızıldere (Özgür, 1998). The only one sulfide precipitation from the hot spring of Babacık in the environs of Kızıldere shows a $\delta^{34}S$ value of -9,63 ± 0,3 (‰) CDT. The range of $\delta^{34}S$ 17,2 to 17,98 ± 0,3 (‰) CDT in sulfate precipitations from the environs indicates a slight increase in comparison to those of geothermal systems of Los Humeros in Mexico (Serrano et al., 1996); thereby, the $\delta^{34}S$ value in sulfide precipitation from Babacik corresponds to the $\delta^{34}S$ values of sulfide precipitation of Los Humeros in Mexico, which can be linked to a magmatic origin (Fig. 3).

The sulfate concentrations in hydrothermal fluids can be derived from a marine origin, e.g. ocean water, formation water, and solutions of evaporites, and are generated by oxidation of sulfide minerals which can be precipitated as sulfide mineral phases due to magmatic activity (e.g. Balderer, 1985; Fontes and Michelot, 1985). The origin of sulfate contents in thermal waters might be elucidated by using stable isotope values of $\delta^{34}S$ and $\delta^{18}O$; e.g. $\delta^{18}O$ values > 7 up to 8 (‰ SMOW) indicate a marine origin (Claypool et al., 1980).

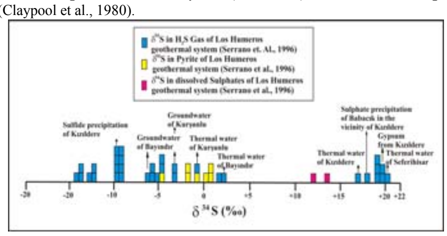

Fig. 3: Isotope ratios of $\delta^{34}S$ in sulfate and sulfide precipitations of thermal waters from Kızıldere, Bayindir, Salihli and Seferihisar. Ratios from Los Homeros are shown for comparison.

The stable isotope ratios of $\delta^{34}S$ and $\delta^{18}O$ in sulfate precipitations of Kızıldere and its environs fall on the field of Pliocene and Miocene evaporites (Pearson et al., 1991) as well as on the field of barytes in metamorphic rocks of Switzerland (Claypool et al., 1980; Fig. 4). The sulfide minerals in hydrothermal sphere which has been defined distinctly due to values of $\delta^{18}O$ in fluid inclusions of quartz samples as gangue minerals of associated sulfide ores can be oxidized by the meteoric groundwaters and thermal waters at the surface in accordance with Fontes and Michelot (1985: in: Özgür, 1998).

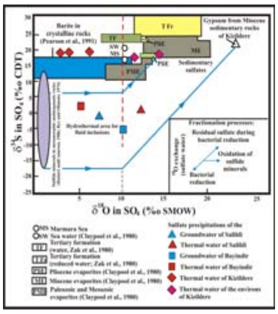

Fig. 4: $\delta^{34}S$ versus $\delta^{18}O$ in sulfate precipitations of groundwaters and thermal waters from Kızıldere, Bayindir, and Salihli. o : samples from Seferihisar.

For comparison, the $\delta^{34}S$ ratios of Hg, Sb, and As ore minerals from Haliköy, Emirli, and Küre in the rift zone of the Kücük Menderes establish a magmatic origin of sulfur due to their isotopic composition from -5,5 to +4,5 (Fig. 5; Özgür, 1998; Gökce and Spiro, 1995).

DISCUSSION

In the basement of the thermal field of Kızıldere, metamorphic rocks occur which are overlain by Pliocene sediments and disrupted by basic towards acidic volcanics proven by $^{3}He/^{4}He$ ratios (Gülec, 1988; Ercan et al., 1995). The rocks in the investigated area are distinguished by sulfide ore

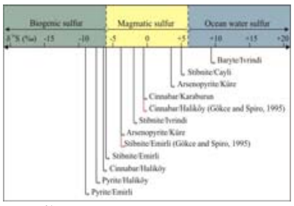

Fig. 5: Isotope ratios of $\delta^{34}S$ in sulfide ore minerals of Haliköy, Emirli, and Küre.

mineralizations which can be established by drill cores of two reinjection wells at a depth of 2.000 m in Tekkehamam and 2.236 m in Kızıldere. Due to the results of $^{87}Sr/^{86}Sr$ ratios, the metamorphic rocks, especially gneiss, of Kızıldere and environs have an intensively fluid-rock interaction (Özgür, 1998). Additionally, there is a fluid- rock interaction between basic towards acidic subvolcanic rocks and thermal waters supported by $^{3}He/^{4}He$ ratios and local occurrence of active geothermal systems and epithermal mineral ore deposits (Özgür, 1998). The basic towards acidic subvolcanic rocks in the area of Kızıldere are useful for heating of thermal waters in meteoric origin established by $\delta^{18}O$ and $\delta^{2}H$ ratios. Moreover, ^{3}H values of thermal waters from Kızıldere lie below detection limits indicating old ground waters with ages of more than 50 years (Özgür, 1998). The isotopic ratios of $\delta^{34}S$ and $\delta^{18}O$ in sulfate precipitations of thermal waters from Kızıldere and its environs establish that sulfur out of magma reaches the metamorphic, sedimentary and magmatic rocks in terms of volatile components (SO_2, H_2S, etc.), precipitates as sulfide minerals, later on, and/or encounter a transformation to sulfate in thermal water reservoir by a disproportionation (e.g. Arnorsson et al., 1983; Saki and Matsubaya, 1977; Fig. 6).

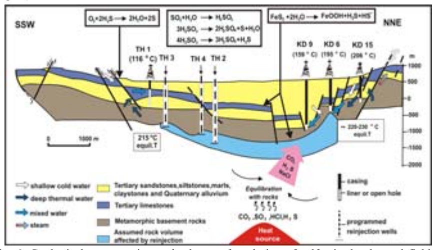

Fig. 6: Geological cross-section and scheme of evolution of sulfur in the thermal field of Kızıldere and environs.

The sulfide minerals of magmatic and diagenetic origin in thermal field of Kızıldere and environs can be oxidized at a depth of near surface spheres. $\delta^{34}S$ ratios can increase in residual sulfates during fraction processes by reduction (Fig. 4), for which sulfur bacteria might be responsible. Thereby, the light sulfur and oxygen isotopes are consumed by sulfur bacteria preferentially whereas the heavy sulfur and oxygen isotopes are enriched.

Additionally, the magmatic origin of sulfur can be corroborated by the ratios of $\delta^{13}C$ and $\delta^{11}B$ as well as by $\delta^{34}S$ in sulfide minerals of Hg, Sb, and arsenopyrite-Au deposits of Haliköy, Emirli, and Küre in the continental rift zone of the Kücük Menderes (Fig. 5; Özgür, 1998). The gypsum occurrences in Pliocene sedimentary rocks and pyrite ore minerals can be added as second source of SO_4^{2-} in thermal waters of Kızıldere and its environs. In dissolution of gypsum by meteoric waters, the atoms of SO_4^{2-} ions in high temperature geothermal systems may equilibrate with those of H_2O (Chiba and Sakai, 1985) which can probably explain the relative low isotope ratios of $\delta^{18}O$ in the thermal waters of Kızıldere compared with the other thermal fields of Bayindir, Salihli, and Seferihisar.

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