

Partitioning of rare earths and some major elements in the Kizildere geothermal field, Turkey

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Received 4 December 2006; accepted 18 October 2007

Available online 21 December 2007

Abstract

Rare earth elements and yttrium (REY), Na⁺, K⁺, Cl⁻, and Ca²⁺ were determined in water, steam, mineral scale and rock samples from the Kizildere geothermal field, Turkey. The CO₂-rich parent fluid originates from a sequence of mica schists with marble intercalations. The chemistry of the parent fluid varies with location and time. The average REY composition of the fluids is derived by extrapolation to the lowest Ca concentrations. The apparent vapor–liquid partitioning factors for REY at 145 °C and 5 bar total absolute pressure are about 0.2, whereas for Ca²⁺, Na⁺, K⁺ and Cl⁻ they are <0.05, about 0.0005, 0.0005 and about 0.02, respectively. Apparent scale–liquid distribution coefficients for REY at 145 and 190 °C are about 0.15 and 0.55, whereas at 100 °C they increase from 0.3 (La) to 1.5 (Lu).

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Keywords: Rare earth elements; Yttrium; Vapor–liquid partition; Scale–liquid distribution; Geothermal fluid; Water/rock interaction; Kizildere; Turkey

1. Introduction

Rare earth element (REE) abundances in the nmol/kg to pmol/kg range have been reported for fumaroles in the Larderello-Travale and Phlegrean Fields areas in Italy (Michard and Albarede, 1986), for the Valles Caldera, NM, USA (Michard, 1989), and for the Salton Sea geothermal

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field, CA, USA (Lepel et al., 1989; Michard, 1989). In contrast, REE and yttrium (REY) abundances in acidic geothermal fluids with pH values between 1.4 and 4.2 were shown to range from $\mu\text{mol/kg}$ to nmol/kg (Honda et al., 1989a,b; Kikawada et al., 1993; James et al., 1995; Lewis et al., 1998). Aggarwal et al. (1996) reported REE abundances in the 0.03–0.4 nmol/kg range in filtered (0.45 μm), pH 6–8, Icelandic geothermal waters. Neutral-to-alkaline spring waters associated with the Idaho Batholith, ID, USA, contain 5–14 pmol/kg , with the less abundant elements not analyzed. In these waters, CO_3^{2-} and OH^- complexes are considered to be the dominant REE and Y species at thermal spring emergence temperatures, whereas under source conditions OH^- complexes predominate (Middlesworth and Wood, 1998). The trends of REE patterns of the acidic (pH 2–4), 70–93 °C Yellowstone (WY, USA) waters are controlled by potential complexing ligands such as Cl^- , F^- , sulfate, and pH (Lewis et al., 1998).

A study of the Larderello-Travale geothermal system revealed complete REE patterns including Y (henceforth referred to as REY) in the range 0.01–5 pmol/l , with vapor–liquid partitioning factors of about 0.2 (Möller et al., 2003). In general, the REY abundance patterns of the geothermal fluids differ significantly from that of their host rocks (Möller and Giese, 1997; Möller et al., 2006). REY distribution is controlled by the solubility of easily accessible REY-bearing minerals, by ion exchange with rock-forming minerals, or by adsorption onto mineral surfaces and their coatings.

REY have been, and still are, considered as natural analogs of individual actinides; for example, Nd is considered an analog of Am and Cm in radioactive waste. REE have therefore been studied in saline groundwaters (Lepel et al., 1989), although the authors admit that very little is known about REY volatility (and hence actinide volatility) under natural conditions.

Geothermal systems are an ideal large-scale experimental setting for studying REY distribution between solids, liquid and vapor under a wide range of temperatures and pressures. Although high flashing rates prevent us from determining the thermodynamic distribution equilibria of elements between the various phases, in these systems we can still study element distribution during boiling and exsolution of gases. Boiling occurs in the earth's crust as a consequence of tectonically induced pressure release. The escaping vapors may condense to form a new liquid with a different chemical composition from that of the parent fluid. For instance, on the basis of their co-precipitated REY contents we expect to distinguish between Ca minerals derived from parent fluids and those obtained from the condensate after boiling.

The CO_2 -rich water-steam system at Kizildere, Turkey, provides a good opportunity for studying REY partitioning between (i) CO_2 -rich liquid- and water-saturated CO_2 vapor and (ii) CO_2 -rich liquid and mineral scale formed under flashing conditions. Based on scale-liquid distribution factors, we can calculate backwards to the composition of the parent fluid under reservoir conditions. The REY patterns of the derived parent fluid are then used to characterize the source rock types. The presence of carbonate scale greatly restricts our ability to sample liquid and vapor from the wellhead cyclone separator because of dissolution of scale particles in cooled liquid and condensed vapor that are both undersaturated with respect to carbonates.

2. Geologic and hydrogeologic setting of the Kizildere geothermal field

The Kizildere field is part of the geothermal area near to the junction of the Gedez and the Büyük Menderes Graben bordering the Menders Massif to the south and east (Fig. 1a). The Menderes Massif, the oldest geological structure on the Anatolian continent, comprises gneisses and schists overlain by marbles, phyllites, metaplutonites and metasedimentary rocks associated with limestones. As a result of the Bozdag uplift, very thick and coarse-grained alluvial and fluvial Pliocene-Quaternary sediments accumulated in the Küçük Menderes and Büyük Menderes

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