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# The behaviour of trace and rare earth elements (REE) during hydrothermal alteration in the Rangan area (Central Iran)

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ABSTRACT

The rhyolitic dome in the Rangan area has been subjected to hydrothermal alterations by two different systems, (1) A fossil magmatic–hydrothermal system with a powerful thermal engine of a deep monzodioritic magma, (2) An active hydrothermal system dominated by meteoric water. Based on mineralogical and geochemical studies, three different alteration facies have been identified (phyllic, advanced argillic and silicic) with notable differences in REE and other trace elements behaviour. In the phyllic alteration zone with assemblage minerals such as sericite, pyrite, quartz, kaolinite, LREE are relatively depleted whereas HREE are enriched. The advanced argillic zone is identified by the presence of alunite–jarosite and pyrophyllite as well as immobility of LREE and depletion in HREE. In the silicic zone, most of LREE are depleted but HREE patterns are unchanged compared to their fresh rock equivalents. All the REE fractionation ratios $(La/Yb)_{cn}$, $(La/Sm)_{cn}$, $(Tb/Yb)_{cn}$, $(Ce/Ce^*)_{cn}$ and $(Eu/Eu^*)_{cn}$ are low in the phyllic altered facies. $(Eu/Eu^*)_{cn}$ in both advanced and silicic facies is low too. In all alteration zones, high field strength elements (HFSE) (e.g. Ti, Zr, Nb) are depleted whereas transition elements (e.g. V, Cr, Co, Ni, Fe) are enriched. Geochemically speaking, trace and rare earth elements behave highly selective in different facies.



## 1. Introduction

Rare earth elements (REE) were often accepted as rather immobile elements, but more recent studies have shown that they can be mobilized by hydrothermal fluid circulation (Alderton et al., 1980; Michard and Albarede, 1986; Palacios et al., 1986). Lately, numerous studies have been carried out on the geochemistry of REE in hydrothermal systems (Lottermoser, 1990; Hopf, 1993; Arribas et al., 1995; Fulignati and Sbrana, 1998; Terakado and Fujitani, 1998; Chang-bock et al., 2002). Felsche and Herrmann (1978) found that most REE are transported in alkaline solutions as carbonate, sulphate or fluorine complexes. Some other workers concluded that the REE mobility is significantly controlled by the availability of complexing ions such as $CO_3^{2-}$, $PO_4^{3-}$, $F^-$, $SO_4^{2-}$ and $Cl^-$, as well as low pH and high rock/water ratio (Michard, 1989; Wood, 1990; Haas et al., 1995).

According to Pirajno (1992) and Takahashi et al. (2004) heavy rare earth elements (HREE) form more stable complexes with some ligands and stay in solution longer than light rare earth elements (LREE). Therefore, they tend to concentrate in later products of hydrothermal systems. In this context, some investigators focused on REE behaviour in different alteration facies. Taylor and Fryer (1980) identified multiple-stage hydrothermal altered zones in the porphyry copper deposits in Turkey and stated that REE distribution in unaltered and altered rocks can be taken as an evidence of changing fluid conditions from dominantly magmatic to dominantly meteoric.

The works of Taylor and Fryer (1982, 1983) demonstrate that in the potassic alteration of a porphyry system, LREE are relatively immobile whereas HREE are strongly depleted. Also, from propylitic to phyllic alteration or with decreasing $K^+$ activity and increasing $H^+$ metasomatism an overall depletion of REE is noticed. This reduction is more pronounced for LREE than for HREE. In contrast, Terakado and Fujitani (1998) came to the conclusion that under strongly acidic hydrothermal conditions, some REE are retained in the rocks and the alunite in their study area is characterized by LREE enrichment.

Fulignati et al. (1999) studied REE distribution in the alteration facies of the magmatic–hydrothermal system of La Fossa Vulcano (Aeolian Islands, Italy) and found remarkable differences in the REE behaviour in different alteration facies. These elements are strongly depleted in silicic and advanced argillic rocks whereas they are relatively immobile in intermediate argillic, phyllic and propylitic zones. Also, a number of studies have been published pertaining to the significance of REE for exploration (Arvanitidis and Richard, 1986; Ganzeyev et al., 1987; Whitford et al., 1988; Qi-Cong and Cong-Qiang, 2002; Weimin et al., 2003). Based on

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these studies, the ore bodies prospective for metal mineralization might have a distinctive REE signature and therefore, they may have some applications for exploration.

On this account, it appears that the REE behaviour in an aqueous or hydrothermal environment is complex and no simple rules can be established for their mobility during hydrothermal processes. In the present study, we document the effect of hydrothermal alteration on the rhyolitic – dacitic dome southwest of Ardestan, some 70 Km northeast of Isfahan, Iran (Fig. 1), which is supposed to be an epithermal system, investigate the behaviour of REE and ore forming elements in different alteration facies and determine a tentative pattern for their mobility in the study area.

## 2. Geological setting

According to Stocklin (1968), Rangan area is situated in the Central Iranian tectono-sedimentary unit, forming a part of Tertiary Sahand-Bazman or Uromieh-Dokhtar volcanic belt (Fig. 1). The Laramide orogeny (late Cretaceous) created a regional unconformity at the base of Eocene deposits throughout a vast part of Iran. Following this orogeny, and as a result of extensional movements, active basins formed in which a great thickness of basaltic lava to acidic flows and pyroclastic rocks were deposited. Meanwhile, a series of fracturing and folding events were produced by the Laramide orogeny. Flexural slip and drag folds are the main fold types of the area. The Marbine-Rangan fault, trending NW-SE and cross-cutting the main Qom-Zefreh fault (QZF) (Fig. 2), had a significant role in creating the structural framework of the region (Emami and Radfar, 2000).

The predominant rock types of the area are andesite, dacite, rhyolite, tuff and ignimbrite with a minor amount of basalt, all related to the Eocene volcanic activity. The intrusive suites are composed of diorite to monzodiorite and have successively intruded into the volcanic rocks during the post- Oligocene period. The oldest exposed rocks in the studied area are quartz sandstones, black shales and yellow to grayish dolomitic limestones of the Triassic period followed by Jurassic shales and lower Cretaceous limestones. Meanwhile, a dome-shaped rhyolitic lava developed during Eocene time. This unit trends NW-SE parallel to the main direction of the QZF and has subjected to hydrothermal alteration. Two different systems have been involved in its formation: (1) a fossil magmatic–hydrothermal system, which is a major contributor to the system. This system has provided a powerful thermal engine generated by consolidation of a deep monzodioritic magma and has driven hydrothermal circulation which has led to the alteration of dacitic dome during post-Oligocene (Fig. 2). Incidentally, the Jurassic shales and Cretaceous limestones have been locally metamorphosed into hornfels and skarn.

(2) An active low-T hydrothermal system evidenced by the hot springs that were responsible for precipitation of calcium carbonate (Travertine) along the western margin of rhyolitic dome (Fig. 2). The tectonic movements and the QZF in particular, have had a major role in the development of an active meteoric system and in the infiltration of meteoric waters into the rhyolitic rocks of the study area.

Based on field observations, as well as mineralogical and geochemical studies, three different hydrothermal facies (phyllic, advanced argillic and silicic types) are recognized in the Rangan area. The general features of these zones are briefly described in the following sections.

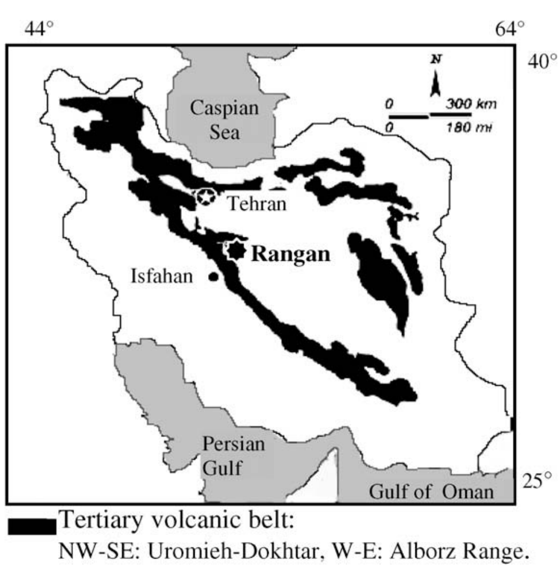


**Fig. 1.** Geographical map of Iran and study area in the Uromieh-Dokhtar belt.

## 3. Sampling and analytical methods

### *3.1. Sample collection*

A total of 70 rock samples were taken. Several unaltered rocks were collected from fresh surface outcrops in order to determine the nature of the original rocks. Characteristics such as grain size, mineralogy, colour, freshness or alteration of samples were described in the field (Fig. 2).

### *3.2. Analytical methods*

The mineral assemblages were analyzed by optical methods in combination with X-ray (powder) diffraction analysis at the Center of Analysis and Test in the University of Isfahan. Several samples of each alteration zone as well as unaltered samples were crushed to less than 200 meshes by using a steel mortar. Major elements were determined by X-Ray Fluorescence Spectrometry (XRF). Sample powders were digested by hydrofluoric and nitric acid (1:1). REE and trace elements were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) by Amdel Ltd. in Australia. For quality control, the International Standards AMH-1 and OU-3 were used as standard samples.

The mineral composition of the advanced argillic mineralogical assemblage was determined using a Cameca SX50 electron microprobe at the University of Oklahoma, Norman (USA). Analytical conditions for the sulphates were 20 kV accelerating voltage, 10 nA beam current and 20 μm defocussed spot size. All elements were counted for 30 s on peak except for Fe (45 s), Mn (45 s) and Sr (60 s). These methods yielded minimum detection levels in the 0.02–0.05 wt% oxide range for all components except for Ba (0.08 wt% BaO), Sr (0.08 wt% SrO) and S (0.08 wt% SO3) calculated at 3-sigma above mean background. The results of the analyses were presented in Tables 1 and 2.

## 4. Field relations and petrographic studies

Based on field studies and their petrographic characteristics, the parent rhyolitic rocks of the study area, have been subjected to post magmatic–hydrothermal alteration processes resulting in phyllic, advanced argillic and silicic facies.

### *4.1. Field relations*

Different hydrothermally altered zones in the study area display various colours. The phyllic alteration is widespread in the east of the rhyolitic dome unit (Fig. 2). This altered zone is characterized