Journal of Applied Geochemistry
Vol.5 No.1 (2003) pp 26-30

# RARE EARTH AND TRACE ELEMENT MOBILITY ACCOMPANYING TOURMALINISATION: EVIDENCE FROM JHUNJHUNU, RAJASTHAN, INDIA

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## Abstract

The paper describes the mobility of trace elements including REE during hydrothermal alternation processes leading to tourmalinization and copper mineralsiation in the acid volcanics of Jhunjhunu area, Rajasthan. The granites and the acid volcanics belong to the Malani igneous suite of rocks.

During tourmalinization there is decrease in silica with subsequent increase in alumina. There is an overall depletion of REE in acid volcanic and granites, and also depletion in Zr. During potash metasomatism there is an increase K, Rb, Zn, Cu, and sodic metasomatism leads to increase in Na, Fe, and enrichment of Rb, Th, Nb. A model of subvolcanic alternation has been suggested for the tourmalinization and the copper (malachite) and specularite malachite mineralsiation.

*Keywords :* REE, Trace elements, Hydrothermal alternation, Mobility, Tourmalinization, Jhunjhunu, Rajasthan.

## 1. Introduction

The paper describes mobility of trace elements including rare earths during hydrothermal alteration processes leading to tourmalinsation and copper, tin mineralsiation in Jhunjhunu area, northeastern Rajasthan and is located in the northwestern part of the Indian shield (Toposheet No. 44p/8; 1: 50,000) 220 km SW of Delhi.

The lithology around Jhunjhunu includes alkali feldspar granite, rhyolite, welded tuff, brecciated tuff rhyolite dykes and, belong to the Malani igneous suite. These rocks occur as radial dykes and volcanoplutonic arcuate intrusions (Sharma 1992, 1994; Kochhar and Sharma, 1992).

## 2. Petrographic Description

Alkali-feldspar granites : The granites vary in colour (pink to grey), grain size (coarse to medium grained), and texture (granophyric and perthitic). They are hypersolvus to subsolvus. Phenocrysts of shattered and embayed quartz, sericitised orthoclase and biotite are common. The accessory minerals are ilmenite, apatite, zircon and tourmaline.

### 2.1 Rhyolite

Rhyolite is medium to fine grained, hard, compact and pink. The essential minerals present in abundance are high quartz, alkali-feldspar, biotite, chlorite, specularite and tourmaline. The accessory minerals are zircon, magnetite. The rhyolites show prophyritic and devitrified textures.

### 2.2 Geochemistry

The Jhunjhunu magmatism is peraluminous and grades from highly fractionated I - type to A-type. The granites are high in silica, alkalies ($Na_2O$ +$K_2O$), Ga/Al, Fe/Mg, Zr, Rb, Ba, U, Th and total REE, low in Ca, Mg, Sr and very low in Hf, Ta, Sc, Co, Cr, Ni and V. The chondrite normalized REE pattern shows relative enrichment of LREE and depletion of HREE (La/Yb : 9) with significant negative Eu anomaly (Fig. 1). The total REE content of granites is more than that of rhyolitics. This may be attributed to the general tendency that the concentration of REE decrease in the later phases of magmatic differentiates, or it may be due to the hydrothermal alternations that these rocks have undergone (Kochhar and Sharma, 1992; Kochhar, 2000). The granites have been classified as high heat production granites (HHP) due to high abundances of radio-active elements (Sharma, 1994).

## 3. Occurrence and Distribution of Tourmaline

In the Malaya ki Dani hill (Nehra Pahar) various stages of development of tourmaline 'suns' in a zone measuring 4 to 5 meters has been observed. The greyish blue variety of rhyolite which is devoid of tourmaline passes through a zone of pinkish grey rhyolite where the tourmaline in the form of stars start appearing in pink.

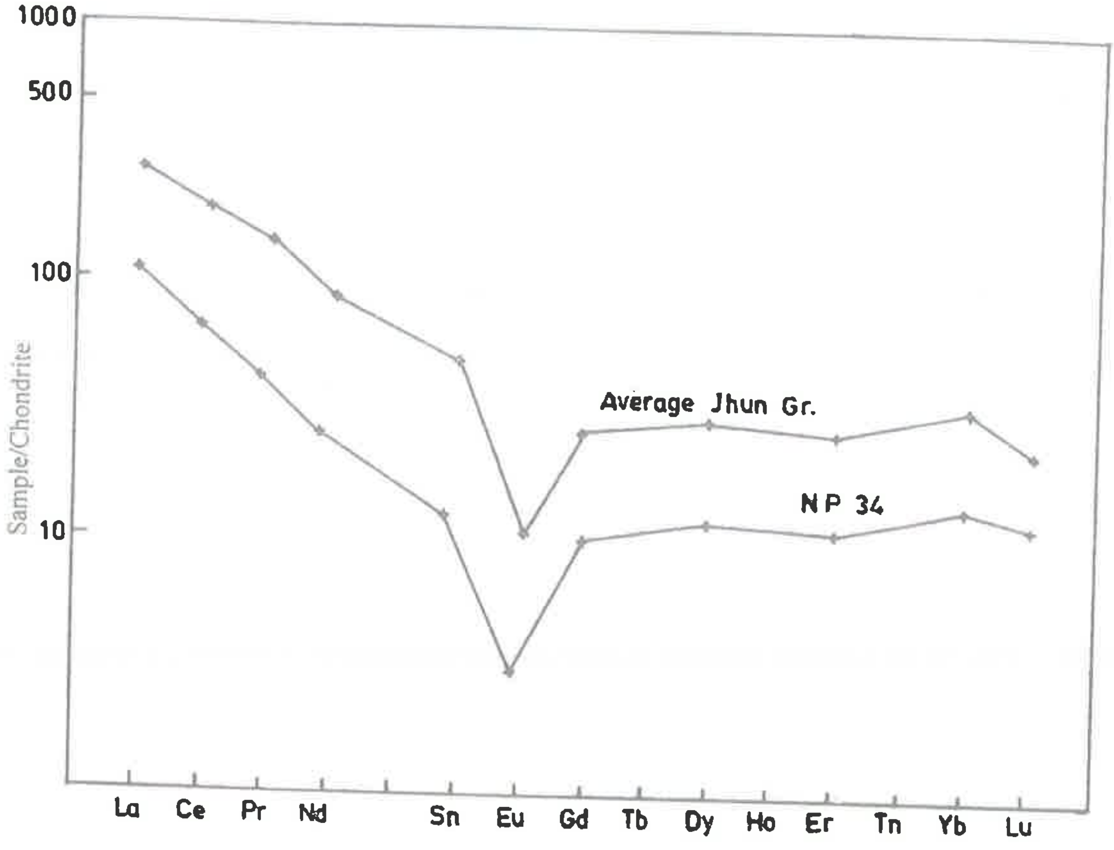


Fig. 1. Chondrite normalized REE plot of Jhunjhunu average granite and granite with tourmaline suns (NP 34).

Present work shows that tourmalinisation resulted in the decrease of silica (about 19%) with concurrent increase in alumina (9%) and iron following the breakdown of biotite. Zr is depleted because of the replacement of zircon by Zr-poor tourmaline; high concentration of boron breaks zircon during alternation and form complex anions with Zr ($ZrF_6^{-2}$) and thus removing the excess of later in solution (Alderton et al., 1980), which may inturn affect the REE mobility, as zircon can accommodate significant concentration or REEs.

Fig. 2 Illustrates the variation in some of the elements from fresh rhyolite (Md4) to mildly tourmalinised (Md 5) to highly altered and completely tourmalinised rhyolite (Md 7).

Potash metasomatism is accompanied by the secondary growth of orthoclase at the expense of biotite and plagioclase feldspar which resulted in the increase of K, Rb, Zn, and Cu. This process was followed by the calcic metasomatism marked by the appearance of calcite and increase in Ca and Sr and loss of Ba to the circulating fluids.

Lastly the sodic metasomatism took place. This resulted in the increase of Na and Fe and substaintial increase in Rb, Th, Nb, La and Ce and depletion in Zr and Y.

Fig. 3. shows the chondrite normalized patterns of normal rhyolite (Md4), pink rhyolite (Md 5) where tourmaline has started developing and completely tourmalinized rhyolite where suns of tourmaline have developed (Md7). There is an overall decrease of the rare earth from Md4 to Md7. This can partly be explained by the dilution effect of newly recrystallyed quartz. But the overall negative Eu anomaly is retained in the process. This can be explained by the rhyolite with profuse development of tourmaline stars. The green ovules of malachite are also associated with this.

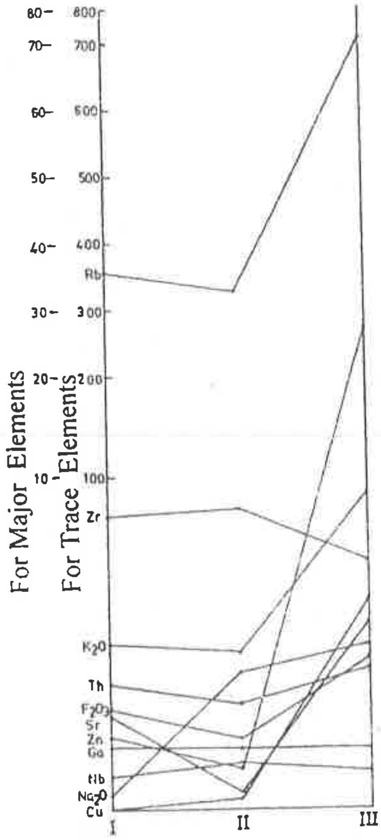


Fig. 2. Geochemical changes from fresh (I) to altered (II) to tourmalinised rhyolite (III) Samples : I : Md 4; II : Md 5; III : Md 7.

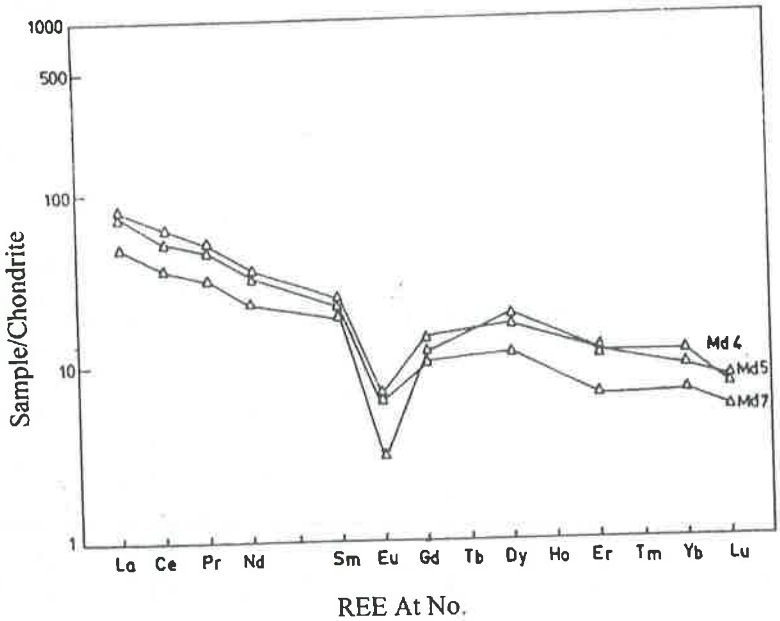


Fig. 3. Chondrite normalized REE plot for Jhunjhunu tourmalinised rhyolites.

Table 1. Chemical data of Jhunjhunu rocks.

| Major Elements | | | | |
|---|---|---|---|---|
| | Rhy | Altered rhy | Tourm rhy | Gr |
| | Md4 | Md5 | Md7 | NP 34 |
| $SiO_2$ | 74.96 | 72.49 | 55.92 | 75.37 |
| $TiO_2$ | 0.18 | 0.13 | 0.23 | 0.36 |
| $Al_2O_3$ | 12.94 | 15.56 | 21.52 | 12.90 |
| $Fe_2O_3$(T) | 2.98 | 2.10 | 4.25 | 2.08 |
| MnO | 0.04 | 0.02 | 0.08 | 0.04 |
| MgO | 0.28 | - | - | 0.30 |
| CaO | 0.20 | 0.10 | 1.29 | 0.79 |
| $Na_2O$ | 0.40 | 4.13 | 4.92 | 1.64 |
| $K_2O$ | 4.88 | 4.71 | 9.61 | 5.30 |
| $P_2O_5$ | 1.00 | 0.04 | 0.46 | 0.01 |

| Trace Elements | | | | |
|---|---|---|---|---|
| V | 15.32 | 6.91 | 46.40 | 7.48 |
| Cr | 4.96 | 5.52 | 59.66 | 5.46 |
| Co | 2.26 | 1.15 | 6.43 | 0.97 |
| Ni | 8.78 | 6.77 | 193.39 | 3.68 |
| Cu | 0.32 | 2.82 | 63.45 | 1.86 |
| Zn | 21.81 | 12.61 | 267.61 | 38.19 |
| Ga | 19.34 | 18.12 | 18.25 | 15.56 |
| Rb | 357.20 | 325.29 | 707.68 | 462.46 |
| Sr | 28.44 | 5.03 | 56.33 | 21.80 |
| Y | 26.87 | 27.04 | 13.62 | 39.54 |
| D | 87.78 | 89.83 | 84.25 | 248.96 |
| Sc | 1.52 | 1.70 | 1.60 | 3.91 |
| Nb | 10.60 | 13.44 | 11.43 | 16.88 |
| Ba | 326.20 | 460.14 | 100.14 | 160.10 |
| HF | 4.38 | 4.69 | 4.41 | 7.54 |
| Ta | 1.87 | 3.07 | 2.89 | 2.16 |
| Th | 38.66 | 32.66 | 42.49 | 66.00 |
| V | 7.34 | 14.98 | 3.58 | 13.66 |

| Rare Earth Element Chondrite Normalised Data (Normalising values after Nakamura, 1974) | | | | |
|---|---|---|---|---|
| La | 80.03 | 49.24 | 76.26 | 118.20 |
| Sc | 67.52 | 36.71 | 53.84 | 85.56 |
| Pr | 51.37 | 30.60 | 46.29 | 67.41 |
| Nd | 36.17 | 22.04 | 33.17 | 47.52 |
| Sm | 25.02 | 19.31 | 22.46 | 26.69 |
| Eu | 6.88 | 2.85 | 6.36 | 5.06 |
| Gd | 14.45 | 12.17 | 10.32 | 15.21 |
| Dy | 17.25 | 18.80 | 11.34 | 17.46 |
| Er | 11.68 | 11.61 | 6.26 | 16.26 |
| Yb | 10.18 | 11.36 | 7.04 | 20.22 |
| Lu | 7.96 | 7.66 | 5.60 | 17.10 |

The material which is transitional between parent rock (Md4) and altered rocks (Md7), altered pink rhyolite (Md5) show following mineralogical features. The groundmass is very fine grained with embayed crystals of quartz and K-feldspar Quartz is fractured and occurs in different shapes like square, triangle etc. Biotite is of brown colour and encloses a few grains of zircon. Plagioclase is altered. Muscovite occurs in the sample Md4. In sample no. Md5, the groundmass is very much altered, green tourmaline occurs, flakes of biotite (brown to green colour) with pleochroic halos occur and also magnetite appears. In Md7, small grains of K-feldspar (of secondary origin) occur in addition to plenty of quartz and plagicolase while tourmaline and muscovite as the dominating ferromagnesian minerals appear. Muscovite at some places surrounds tourmaline, biotite disappears, calcite appears as rhomohedral crystals in places.

Four samples : Md4-rhyolite, Md5 - altered rhyolite, Md7 - tourmalinized rhyolite and NP 34 - and granite (with tourmaline sun) which intruded into rhyolite have been analyzed at NGRI Hyderabad for major elements (by XRF) and trace elements including REE by ICP-MS (Table 1).

Alderton et al., (1980) suggested two stages of allteration. The present study of the chemistry (Table 1) suggests that four alternation processes have taken place leading to tourmalinization, potash-silicate alternation followed by calcic metasomatism and soda metasomatism. Tourmaline and quartz are unable to accommodate all the light REEs released from feldspar and biotite. However tourmaline has sites which can accommodate $Eu^{+2}$ and thus $Eu^{+2}$did not suffer much.

Similarly the sample of granite (NP 34) which shows development 'suns' of tourmaline is relatively impoverished compared to the granties which do not show development or tourmaline (Fig. 1).

Thus REE appear to be mobile during hydrothermal and supergene alterations. They are partly removed from the system during the stage or sericitic alternation, near total stage of sericlic removal during tourmalinsation and during chloritization and argillic (clay) alteration. REE mobility is enhanced by the presence of fluorine in the alternation fluids partly because REE form more stable complexes with F than with CL and partly because elements such as Ti, Zr and P that form REE bearing mineral phases are themselves potentially mobile (Alderton et al., 1980).

A model of subvolcanic alternation for the origin of tourmalines is suggested because of intrusive reationship between rhyolite and granite, brecciateion, alternation and formation of ovules of malachite in the tourmalinsed samples, presence of specularite and high concentration of Sn in these rocks (Kochhar et al., 1991).

**Acknowledgement**

The traces elements including REEs were determined at NGRI, Hydrabad, We are thankful to Dr. S.M. Naqvi for constant encouragement and keen interst shown in our project. Dr. V. Balaram in thanked for his help in analytical work.

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Received on 26-07-01; Revised Ms accepted on 26-07-02