# IMMOBILE TRACE ELEMENTS DISCRIMINATION DIAGRAMMS WITH ZEOLITIZED VOLCANICLASTICS FROM THE EVROS - THRACE - RHODOPE VOLCANIC TERRAIN

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## Abstract

*The Rhodope and Evros areas of the Thrace Region in north-eastern Greece and the adjusted areas in Bulgaria are characterized by wide spread volcanic formations of Upper Eocene to Miocene in age. The volcaniclastic materials associated with such formations have, in some cases, undergone inter alia a notable zeolitization process. The mineralogy of the altered volcaniclastics is often dominated by clinoptilolite - heulandite type of minerals. The Winchester and Floyd (1977) plots indicating rhyodacite/dacite to trachyandesite parent materials, while the similar diagram, as modified by Pearce (1986), indicate andesite to trachyandesite precursors. The alkalinity index (Nb/Y ratio) seems to coincide between the two types of diagrams, but, there is a notable difference of the differentiation index, i.e. the $Zr/TiO_2$ ratio. The Th-Co diagram (Hastie et al., 2007) unfolds a clearer picture for the nature of the precursors and reveals a clear progression of a calc-alkaline to a high-K calc alkaline affinity of the parental volcanic materials.*

***Key words:*** *volcaniclastics, zeolitization, zeolite minerals, geochemical classification, trace elements, Thrace - Evros, Greece.*

## 1. Introduction

Zeolite minerals, such as clinoptilolite and mordenite, are often found worldwide as alteration products in volcaniclastic materials. It is known that the zeolitization involves a diffusion-controlled hydration, mainly of volcanic glass, and an alkali ion exchange procedure. As a result, the zeolitization involves the relative gain and losses of elements initially present, especially alkaline and alkali earths and sometimes Si too. So, because of their zeolitization, these materials usually do not attract any considerable petrological attention, especially on their geochemical nature. The truth is that under this situation, the geochemical nature of the parent materials is extremely difficult to establish. The indiscriminate use of geochemical classification diagrams is not recommended.

The objective of the present study was to choose and apply the most appropriate geochemical tools, for zeolitized rocks, i.e. altered materials, with an ultimate scope to examine their geochemical characteristics and to verify the nature of the parent volcaniclastc materials (i.e. the nature of the precursors for the formation of zeolites).

## 2. Geological setting

The geological structure of the Western Thrace – Evros area of Greece consists of three distinct units:

1. The Pre - Mesozoic crystalline basement which consist of a high grade metamorphic rocks, such as marbles, gneisses, amphibolites and pegmatites (lower allochthonous unit) to schist- and amphibolitic- gneisses and amhibolites (upper autochthonous unit).

2. The Circum-Rhodope Zone, which, in the wider Thrace and Evros areas, consist of two parts, the Makri Unit and the Drymos-Melia Series.

3. Tertiary basins which are built from: a) volcanic rocks, such as granite bodies, sills and dykes, b) volcaniclastic materials such as tuffs, breccias and lahars, and c) sediments and sedimentary rocks such as conglomerates, sandstones, marls, sandy marls and locally lignite seams. The magmatic activity, of Eocene to Oligocene age is related continental collision that followed the subduction of African - Arabian plate beneath the Eurasian (Yanev et. al. 1998). Marchev et al (2004) have compiled a map of the geology of the Eastern Rhodope area (Figure 1).

## 3. Materials and Methods

### 3.1 Materials

The samples we used are zeolite-bearing volcaniclastic materials from the wider Evros - Thrace – Rhodope volcanic terrain of Greece. Typical examples of such type of alteration have been recorded in numerous locations in the above mentioned areas of north-eastern Greece, (Figure 2), as well as in south and southeast Bulgaria (Tsirambides et al., 1989; Kirov et al., 1990; Tsolis-Katagas and Katagas, 1990; Kitsopoulos, 1991; Skarpelis et al., 1993; Djourova and Aleksiev, 1995; Stamatakis et al., 1998; Marantos et al., 2004).

### 3.2 XRD and XRF

Since the mineralogy of the zeolitized materials of the Tertiary basins of the Thrace – Evros area has been examined in many occasions in the past (Tsirambides et al., 1989; Kirov et al., 1990; Tsolis-Katagas and Katagas, 1990; Skarpelis et al., 1993; Djourova and Aleksiev, 1995; Stamatakis et al., 1998; Marantos et al., 2004), the XRD method was applied, with the sole purpose to confirm the presence of zeolite minerals in the samples chosen to be examined.

The geochemistry was examined by using a PANalytical Axios Advanced PW4400 XRF spectrometer, fitted with a 4kW Rh anode SST-mAX X-Ray tube. Major elements determined on fused glass beads prepared from ignited powders sample to flux ratio 1:5, 80% Li metaborate: 20% Li tetraborate flux. Trace elements analysed on 32mm diameter pressed powder briquettes prepared from 10g fine ground powder mixed with ca 20-25 drops 7% PVA soln and pressed at 10 tons per square inch. Various international standards, as recorded in GeoRem (Jochum et al., 2005, http://geo-rem.mpch-mainz.gwdg.de), were run with the samples as control on the quality of the analyses.

## 4. Data

### Data 4.1

The XRD analysis has confirmed the presence, in various amounts, of zeolite minerals in the samples studied. There was no evidence found in their mineralogy in line with any influence of any other significant alteration, i.e. hydrothermal.

Some representative data, on $TiO_2$, Nb, Zr, Y, Th and Co values from the XRF analyses of the ze-olitized volcaniclastics are given in Table 1.
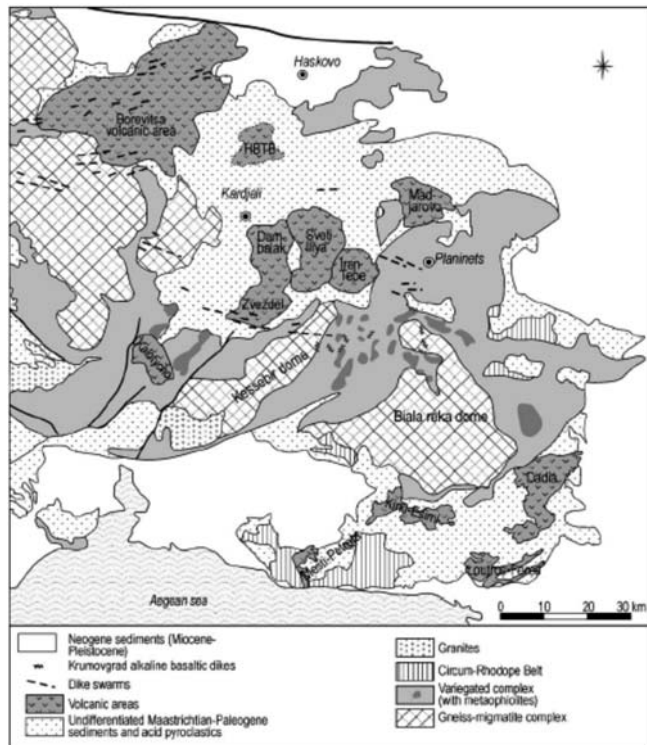
**Fig. 1 :** Schematic map of the geological structure of Eastern Rhodope (Marchev et al., 2004).



**Fig. 2 :** Zeolite deposits (Z) and occurrences (z) in Thrace (north eastern Greece), scale 1:1.000.000 (Marantos et al., 2000).

**Table 1.**

| Sample | Locality | TiO$_2$ | Nb | Zr | Y | Th | Co |
|--------|----------|---------|-----|-----|-----|-----|-----|
|        |          | %       | ppm | | | | |
| **M1** | Metaxades | 0.11 | 28.1 | 60.8 | 34.9 | 21.6 | 0.9 |
| **M2** | Metaxades | 0.09 | 27.7 | 65.9 | 28.4 | 22.7 | 0.9 |
| **L1** | Lefkimi - Dadia | 0.13 | 10.2 | 87.8 | 12.0 | 15.8 | 0..8 |
| **L2** | Lefkimi - Dadia | 0.18 | 8.4 | 91.6 | 18.6 | 14.1 | 3.0 |
| **P1** | Petrota | 0.16 | 21.9 | 145.9 | 16.5 | 30.9 | 0.8 |
| **P2** | Petrota | 0.17 | 26.6 | 166.8 | 22.2 | 38.3 | 0.8 |
| **F1** | Ferres | 0.14 | 8.9 | 65.4 | 13.1 | 12.9 | 1 |
| **F2** | Ferres | 0.40 | 6.3 | 136.2 | 13.1 | 12.3 | 5 |

The classic SiO$_2$ vs. K$_2$O (Peccerillo & Taylor, 1976; Rickwood, 1989) and the SiO$_2$ vs. Na$_2$O+K$_2$O (Le Maitre et al., 1989, 1992) diagrams have been proved unusable with zeolitized materials (Kitsopoulos et al., 2001). In these cases the problems occurred are related to the mobilisation and the redistribution of the alkalis during the zeolitization process. An alternative approach to establish the nature of the parent materials is to use immobile trace elements. As a proxy to the TAS diagram, a discrimination diagram, based on immobile elements, was proposed, which uses the Nb/Y vs. Zr/TiO$_2$ ratios (Winchester and Floyd, 1977). The Ti, Zr, Nb and Y are considered immobile during post-consolidation alteration and metamorphic processes. In the Winchester and Floyd, the Zr/TiO$_2$ ratio can primarily act as a differentiation index, as the differentiation of a basaltic magma can be traced by the decrease of TiO$_2$, and to a less extent as an alkalinity index, as Zr tends to concentrate in alkaline rocks. The Nb/Y ratio acts only as an alkalinity index (Pearce and Cann 1973,) which corresponds with the higher concentrations of Nb in alkaline provinces. The field boundaries of the diagram should be viewed as marking gradational changes rather than sharply defined fields. Also, it should be always taken into account that the diagram was prepared using all types of igneous rocks except for island arc lavas. As the original plot by Winchester and Floyd (1977) has been designed prior to the publication of the TAS diagram by Le Bas et al. (1986, 1992), the field definition has been subsequently modified by Pearce (1996) who used a much larger dataset and also statistically drawn boundaries. The diagram used volcanic arc analyses but it poses the problem of a large overlap displayed by island arc basalts, basaltic andesites, andesites and dacites.

## 5. Discussion - Conclusions

By using the Winchester and Floyd (1977) it can be seen that the samples examined plot in the field of rhyodacite/dacite to trachyandesite, with one sample be plotted as trachyte (Fig. 3). On the similar diagram as modified by Pearce (1986) they plot on the field of andesite to trachyandesite (Figure 4). Although the alkalinity index (Nb/Y ratio) seems to coincide between the two plots, there is a notable difference of the differentiation index of these plots, i.e. the Zr/TiO$_2$ ratio.

Koutles et al. (1995) examined the geochemistry of a single zeolitized outcrop, the Metaxades deposit, by using samples which were collected on a vertical mode, of a traverse of visible thickness of 100m, in the Metaxades quarry. Their results are plotted in the Winchester and Floyd (1977) and the similar, but modified, by Pearce (1986) (Figs 5 & 6).
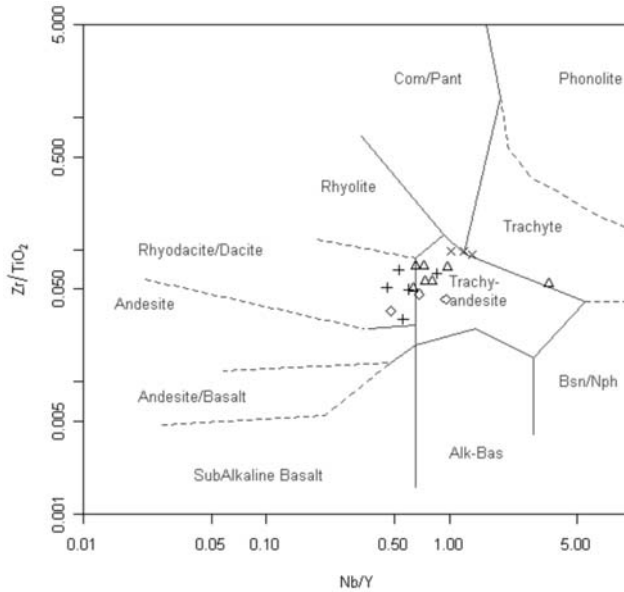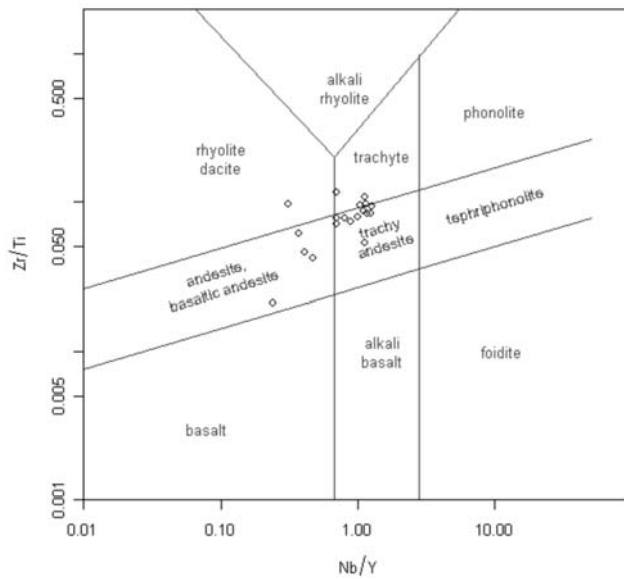
**Fig. 3:** Nb/Y vs. Zr/TiO2 plot of XRF analyses of zeolitized materials on the diagram by Winchester and Floyd (1977). +: Dadia-Lefkimi, Δ: Metaxades, X: Petrota, ◊: Ferres.
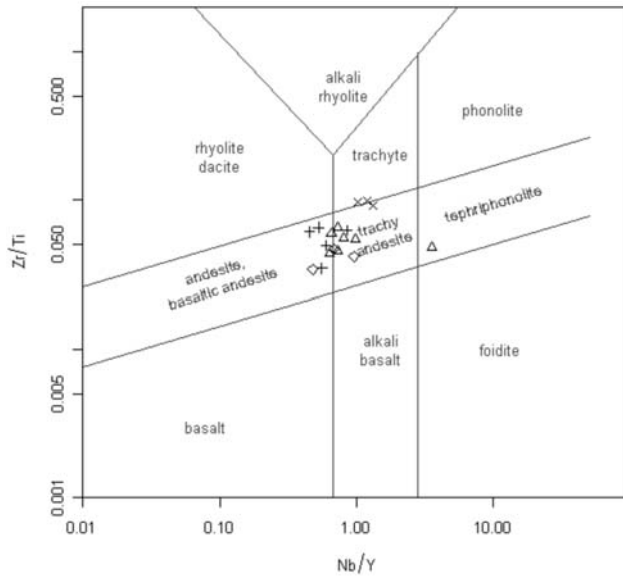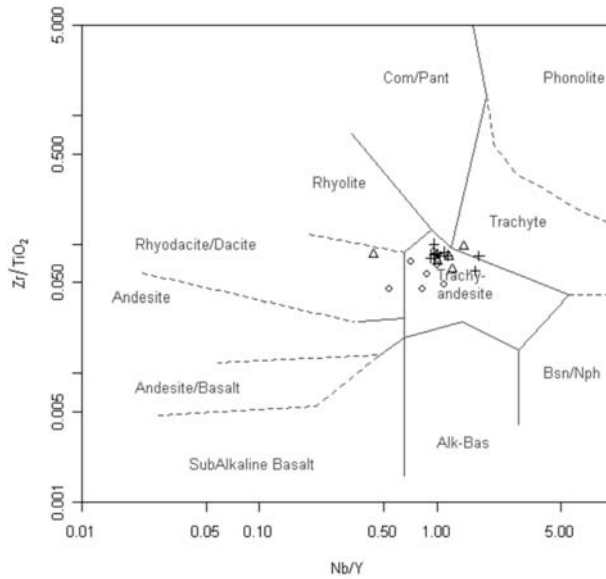


**Fig. 4:** Nb/Y vs. Zr/Ti plot of XRF analyses of zeolitized materials on the diagram by Winchester and Floyd (1977), as modified by Pearce (1986). +: Dadia-Lefkimi, Δ: Metaxades, X: Petrota, ◊: Ferres.
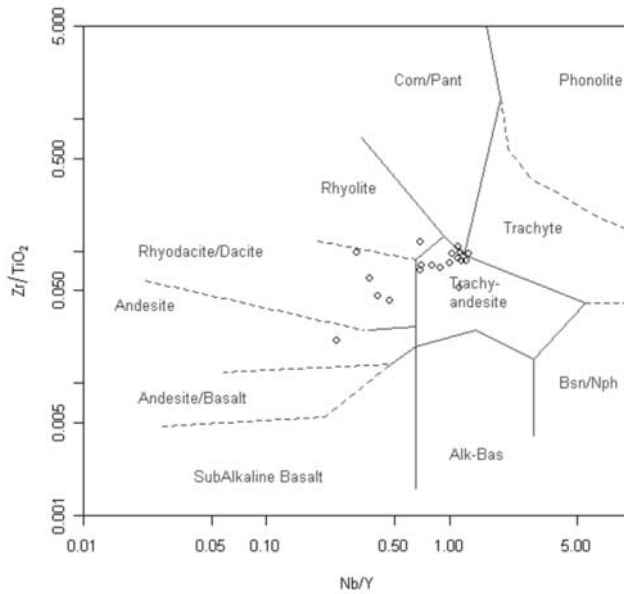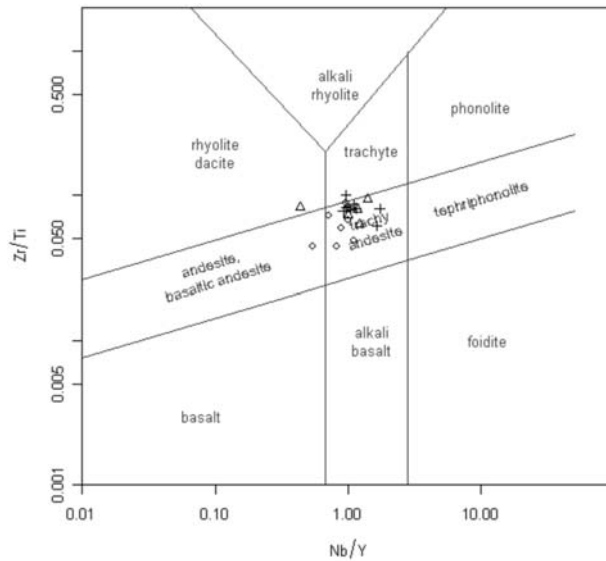
**Fig. 5:** Nb/Y vs. Zr/TiO$_2$ plot of XRF analyses of zeolitized materials from Metaxades, Evros, Greece. Diagram by Winchester and Floyd (1977). Data from Koutles et al. (1995).
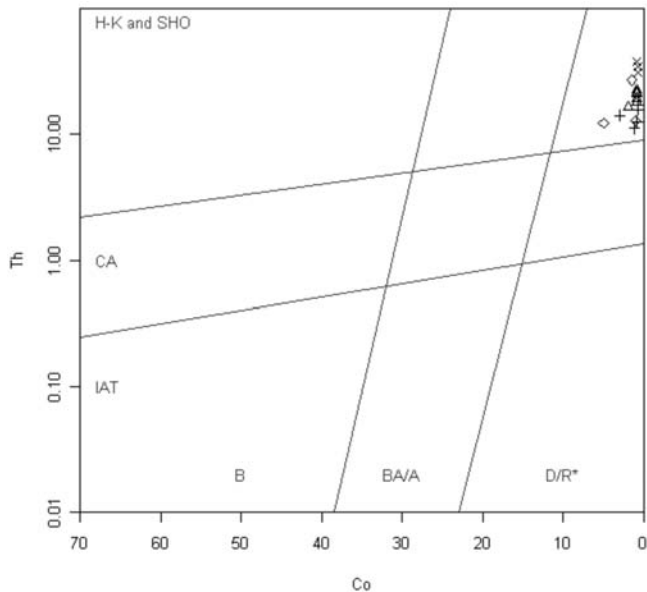


**Fig. 6:** Nb/Y vs. Zr/Ti plot of XRF analyses of zeolitized materials from Metaxades, Evros County, Greece. Diagram by Winchester and Floyd (1977), as modified by Pearce (1986). Data from Koutles et al. (1995).

**Fig. 7:** Nb/Y vs. Zr/TiO$_2$ plot of XRF analyses of zeolitized materials from Pentalofos, Palestra and Petrota-Paleochorofa area. Diagram by Winchester and Floyd (1977). Data from Stamatakis et al. (1998).



**Fig. 8:** Nb/Y vs. Zr/TiO$_2$ plot of XRF analyses of zeolitized materials from Pentalofos, Palestra and Petrota-Paleochorofa area. Diagram by Winchester and Floyd (1977), as modified by Pearce (1986). Data from Stamatakis et al. (1998).

**Fig. 9:** Th - Co plot of XRF analyses of zeolitized materials on the diagram by Hastie et al. (2007). B, basalt; BA/A, basaltic andesite and andesite; D/R*, dacite and rhyolite (* indicates that latites and trachytes also fall in the D/R fields). IAT, island arc tholeiite; CA, calc-alkaline; H-K, high-K calc-alkaline; SHO, shoshonite. +: Dadia-Lefkimi, Δ: Metaxades, X: Petrota, ◊: Ferres.

In both diagrams the spreads, in terms of both the differentiation and the alkalinity indexes, and subsequently of the rock types of the precursor material, are notable. By taking into consideration the fact that there is no evidence in the area of the influence of a significant heavy alteration procedure, for example post hydrothermal events, it seems that these spreads, which come from a single pyroclastic unit with a vertical examined thickness of 100m, are to be questioned. Nb shows a mean value of 24.79 (s.d. 6.24), Zr 68.63 (s.d. 8.18), and Y 33.95 (14.31) respectively.

Stamatakis et al examined the geochemistry of zeolitized outcrops from the Pentalofos-Palaistra-Petrota area. In this case the plots in the Winchester and Floyd (1977) and the one modified by Pearce (1986) are clearly showing an almost single parent precursor (Figs 7, 8).

A quite important diagram used to identify rock types and volcanic series of volcanic are rocks is the $K_2O$ - $SiO_2$ diagram, which however is highly susceptible to the effects of alteration. Working with altered volcanic island arc rocks Hastie et al. (2007) have developed a similar diagram by using Th as a proxy for $K_2O$ and Co as a proxy for $SiO_2$ with a classification success rate of about 80%. They also claimed that they managed to identify the volcanic series of initially hydrothermally altered, then tropically weathered, Cretaceous volcanic arc lavas from Jamaica. There was no indication from the bibliography that the diagram has been ever used with zeolitized volcanics and certainly has not been applied to such materials from Greece. The use of Th and Co has been proved extremely successful with heavily altered, by tropical weathering, hydrothermal and metamorphic processes, lavas comprising of basalts and dacitic tuffs (Hastie *et al*., 2008; Hastie and Kerr, 2010) as well as in calc-alkaline and alkaline magma mixing geo-petrological terrains (Luhr et al., 2010).

In this case it becomes apparent (Fig. 9) that the rock type of the precursor of the zeolitized material studied is narrowed down to the field of dacites/rhyolites. This is coinciding with the finding of the initial Winchester and Floyd diagram. However, the Hastie diagram also reveals a degree of progression of a almost calc-alkaline to a high-K calc alkaline affinity of the parental volcanic materials.

## 6. Acknowledgments

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