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K/Ar GEOCHRONOLOGY AND Sr ISOTOPE GEOCHEMISTRY OF « DACITIC SERIES » FROM EASTERN PONTIC CHAIN (NE TURKEY)

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ABSTRACT. — K/Ar ages and $^{87}Sr/^{86}Sr$ ratios for ten selected acid volcanic rocks from eastern Pontids are herein reported. Results of K/Ar dating point out that both dacite and rhyolite rocks were emplaced in the area during about a 75 m.y. time-span, from Cenomanian up to Oligocene times. As acid volcanites from eastern Pontids were recognized to exhibit close spatial association with the fault system, radiometric ages give first-hand information on the tectonics of this orogenic area. However, probably owing to the limited number of samples which were analysed, no paroxysmal pulses of volcanic and tectonic activity were found.

As regards strontium isotope geochemistry, $(^{87}Sr/^{86}Sr)_i$ ratios ranging from 0.70380 ± 2 to 0.71228 ± 2 were measured. As Sr isotopic composition does not show any correlation neither with age nor silica content of the rocks, the hypothesis of systematic ^{87}Sr effects directly produced by source materials as subducted oceanic slabs can be hardly supported. On the other hand $^{87}Sr/^{86}Sr$ ratios were found to display a positive correlation with the Sr content. As the rocks from study area often contain disseminated sulphide-minerals and hydrothermal calcite, it is hypothesized that mineralizing fluids, enriched in ^{87}Sr through interaction with Mesozoic limestones, produced a secondary contamination which modified the original isotope ratios of the volcanics. In this view the low $^{87}Sr/^{86}Sr$ exhibited by the youngest volcanite, dated at 24 m.y., strongly suggests that at that time hydrothermal processes were already over.

RIASSUNTO. — Vengono presentati i risultati delle determinazioni delle età K/Ar e dei rapporti $^{87}Sr/^{86}Sr$ ottenuti su 10 campioni di rioliti e daciti provenienti dall'area orientale della Turchia (batolite di Rize).

Le età K/Ar indicano che tali rocce sono state messe in posto in un intervallo di 75 M.A., dal Cenomaniano all'Eocene. Le età radiometriche forniscono alcune informazioni preliminari circa le relazioni tra magmatismo ed evoluzione tettonica di quest'area orogenica.

I rapporti isotopici iniziali dello stronzio $^{87}Sr/^{86}Sr_i$ variano da un minimo di 0,70380±2 a 0,71228±2. Poichè non è stata osservata nessuna relazione tra i raporti iniziali dello stronzio e l'età ed il chimismo delle rocce, sembra altamente improbabile che tali rapporti isotopici siano da ricondurre a magmi differenti originati durante la subduzione della placca litosferica turca.

Risulta, al contrario, una buona correlazione tra i rapporti isotopici iniziali dello stronzio ed il contenuto elementare di Sr dei vari campioni. Poichè le rocce dell'area studiata risultano contenere solfuri e carbonati secondari è verosimile che i fluidi responsabili della messa in posto delle mineralizzazioni idrotermali, siano anche i responsabili della variazione osservata nei rapporti isotopici iniziali dello stronzio. In questo modello il basso rapporto iniziale del campione che ha fornito un'età di 24 M.A., potrebbe essere quello originale del fuso magmatico; ciò lascierebbe supporre che i processi mineralizzanti fossero conclusi prima della messa in posto dei prodotti riconducibili a tale magmatismo.

Introduction

According to MC KENZIE (1972) and DEWEY et al. (1973), NE Turkey represents a crucial key area to understand the tectonic evolution of the eastern Mediterranean basin, as it is located where an important branch of Mesozoic Thetys ocean underwent subduction by the northward moving Turkish plate.

We believe that to investigate fruitfully the relationship between tectonics and magmatism of eastern Pontids, which depends on various phases of underthrusting, motion, collision and fragmentation of many local plates, more geochronological support is needed.

Hitherto, absolute chronology dealing with Pontic volcanics was quite inadequate, as only a few radiometric age determinations on poorly spread, feldspathoid-bearing volcanites from Trabzon area have been reported (GUMUS, 1978).

As far as strontium isotope geochemistry is concerned, the picture is by far worst, as in AA. knowledge no data are available.

Such a lack of information likely contributes to the disagreement on the general interpretation of magmatism and tectonics in Pontic chain, despite some accurate petrochemical investigations carried out during the last decade. Petrochemical studies alone, however, may lead to biased conclusions as volcanics often suffered hardly-detectable hydrothermal alteration during the recurrent and wide spread deposition of sulphide-minerals occurred in the area.

The samples analysed for this work consist of dacites and rhyolites emplaced starting in Lower Cretaceous and lasting up to Oligocene times, thus spanning almost totally the Pontic volcanism. Special attention was paid to acid volcanics since they show close spatial association with the fault patterns of this orogenic area.

Geologic setting of study area

On the basis of tectonic evidences KETIN (1966) divided Turkey into four main structural elements which, from north to south, are Pontids, Anatolids, Taurids and the so called Border Folds, this latter representing the beginning of the Arabian platform.

Pontic chain is a wide-extended belt which rims the Black Sea northward and is separated southward from the Anatolids by the impressive North Anatolian Fault. Pontids, considered as a whole, extend eastward to Minor-Caucasus and through Turkey run westward to Bulgaria. Owing to some notable petrographic and structural differences in such a long chain, SAWAMURA (1971), BRINKMANN (1976) and ADAMIA et al. (1980) pointed out the opportunity of dividing the chain into an eastern and a western sector, the border of their respective domains being represented by the N-S fault system close to Samson.

Oldest known rocks, Paleozoic in age, mainly outcrop in the western sector of the belt and, folded as well as metamorphosed to a variable extent, make up the crystalline basement. In particular, as regards eastern Pontids, the basement is formed by granites, gneisses, shales, schists and amphibolites believed to be Permo-Carboniferous in age.

Both marine and continental Mesozoic sedimentary formations overlay the crystalline basement; Triassic is mainly represented by limestones, while neritic carbonate-bearing sediments as well as shales and sandstones were assigned Jurassic age. Its noteworthy that owing to the occurrence of very reliable microfaunal association in the limestones, a satisfactory stratigraphy for the Mesozoic formations has been implemented.

Even though the beginning of Pontic volcanism when discussed in detail may lead to a controversial interpretation, there is general agreement (MAUCHER et al., 1961; AKIM, 1978) in assigning a Cretaceous-Eocene age to the impressive volcano-sedimentary complex which is spread almost all over eastern Pontids.

Main features of Cretaceous-Eocene volcanism are represented by both submarine and subaerial activity, which produced pillow-lava structures, and a discontinuous eruption pattern which made possible marine sediments to be interbedded within volcanics. It was claimed that apart from clastic products Pontic volcanism mainly originated basaltic and andesitic lavas (PECCERILLO and TAYLOR, 1976), acid rocks being by far subordinate. According to AKINCI (pers. comm., 1982), however, on the basis of detailed field work carried out along the E-W transversee Trabzon-Hopa, it is also apparent a notable occurrence of acid volcanics, i.e. from dacites to rhyolites. Owing to this new evidence, in the up to date « Generalized columnar section of the eastern Pontids » (AKINCI, 1982, unpubl.) the so called « Dacitic Series » (namely a unit between the Lower and the Upper basic Series) was greatly emphasized.

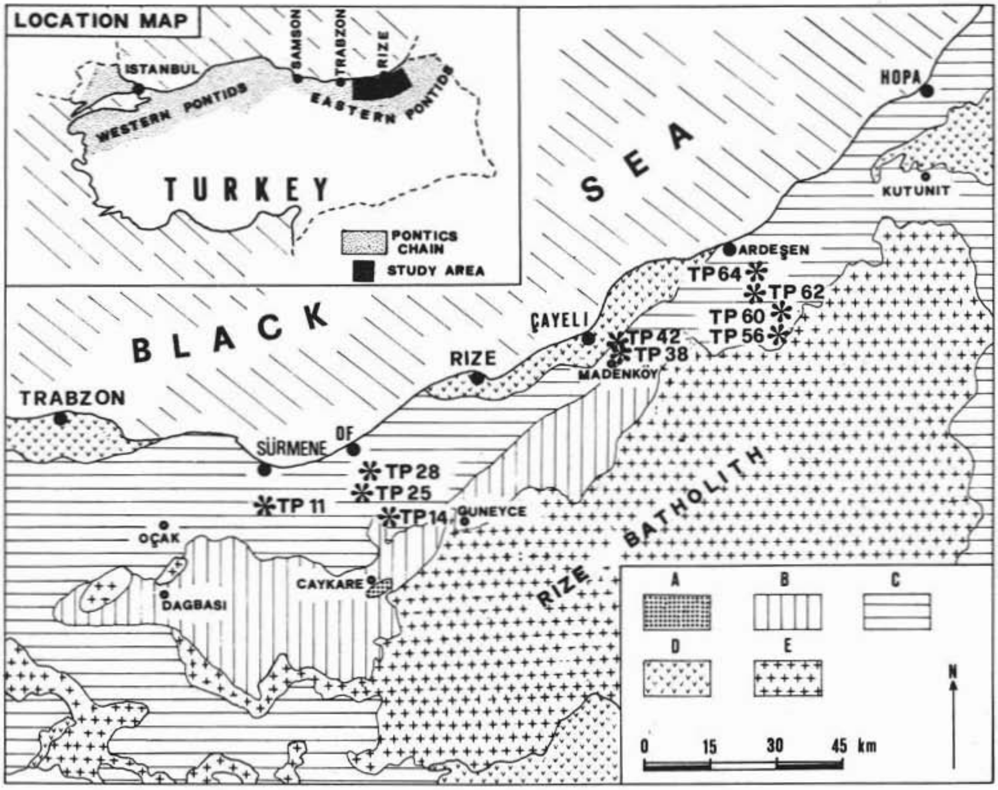

Fig. 1. — Geologic sketch map of the study area. Locations of the sampling sites are indicated by stars. Symbols as follows: A = Crystalline basement; B = Lower basic Series; C = Dacite Series; D = Upper basic Series; E = Intrusive bodies.

Origin and evolution of magmatism in the Pontic belt have been differently discussed. According to Egin et al. (1979) a calc-alkaline suite of Eocene age followed the Cretaceous tholeiitic Series, whereas Manetti et al. (1983) claimed that Cretaceous and Eocene volcanism of the Pontids are quite distinct and unrelated.

Anyhow, in the Upper Eocene and Late Oligocene, that is at the closing phase of the most representative Pontic volcanism, an extensive acid and intermediate plutonism occurred, which through various magmatic pulses lasted up to Early Miocene. A so called « Young volcanic cycle » developed starting in Early Miocene and continuing to Pliocene times. This cycle, however, besides taking place southward relative to the central ridge of Pontids, mainly occurred close to those areas where subordinate plates underwent collision and fragmentation.

Experimental

Major alkali metals were determined by an IL-243 flame spectrophotometer, working with Li as internal standard. Silica, Rb and Sr contents were measured by X-ray fluorescence at the analytical lab of the Geological Survey of Canada. The former element was determined on glassy beads obtained by fusion of finely powdered samples and the latter two on just pressed rock powder pellets. Selected specimens of the whole rocks were crushed and the aliquots with a grain size ranging from 30 to 60 mesh were employed to carry out the radiometric analyses according to the procedure reported by Nicoletti et al. (1977) and Nicoletti (1980). Argon analyses were run with a Micromass VG 1200 spectrometer. Decay constants adopted for age calculations were $\lambda_\varepsilon = 0.581 \cdot 10^{-10}$ A^{-1}

and $\lambda_3 = 4.962 \cdot 10^{-10}$ A^{-1}; while as regards the error calculations the equation after DALRYMPLE and LAMPHERE (1969) was used. Results for routine — check analyses, run on international reference samples (Muscovite P207 and Bern 4M; biotite LP6 and phonolite MZ) fairly matched those reported in literature.

Sr isotopic composition was determined on 0.2 g-samples made carbonate-free prior to carry out the dissolution in platinum crucibles by $HF + HClO_4$ mixture. Sr was first separated from the other elements by cation-exchange resin DOWEX 50W X8, and then placed as $Sr(NO_3)_2$ onto a ribbon of Ta in the source of VG Micromass 54 E mass spectrometer. Values for $^{87}Sr/^{86}Sr$ were normalized to a $^{87}Sr/^{86}Sr$ ratio of 0.1194 and recalculated to SRM $SrCO_3$ standard value of 0.71017. Repeated analyses for the SRM standard run during this study yelded a mean $^{87}Sr/^{86}Sr$ ratio of 0.71023 ± 0.00002 (2σ).

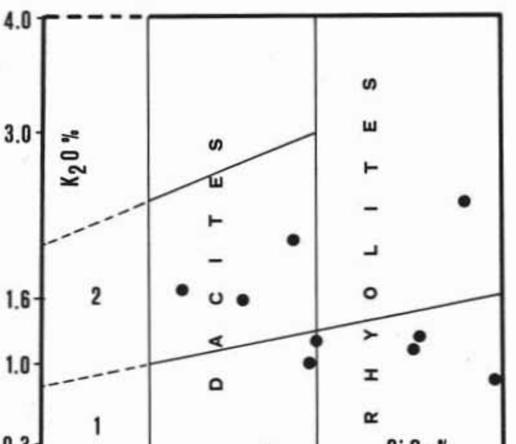

Fig. 2. — K_2O vs. SiO_2 plot for the studied rocks. Boundaries between different fields are after PECCERILLO and TAYLOR (1976). - 1 = island-arc tholeiitic field; 2 = calc-alkaline field.

TABLE 1

Silica contents and K-Ar ages

Sample	SiO2	K%	40Ar rad/g*E-6	40Ar rad%	age(m.y.)
TB-38	64.3	1.415	2.484	47.5	45+2
TB-11	66.8	.708	2.655	75.7	95+3
TB-28	68.0	.233	.924	30.3	101+4
TB-14	68.9	1.910	4.665	63.3	63+3
TB-56	69.7	.910	2.659	42.4	75+3
TB-25	70.0	1.149	2.209	53.2	49+2
TB-60	73.6	1.133	1.053	14.0	24+2
TB-62	73.7	1.240	3.309	58.7	68+3
TB-64	75.5	2.097	7.523	76.4	91+4
TB-42	76.7	.812	2.336	67.0	74+2

Results and discussion

Sampling was carried out along four transverses across the Pontic chain; sampling sites are indicated in fig. 1. Particular care was paid in selecting fresh rock specimens to minimize both weathering and hydrothermal alteration effects.

As usually reported for volcanites from orogenic areas, rock classification on petrological and mineralogical basis is really difficult to implement, owing to the occurrence of fine-grained, hardly-resolvable groundmass. Therefore, taking advantage by the sufficiently broad variation in both SiO_2 and K_2O, rock samples were classified according to the scheme proposed by PECCERILLO and TAYLOR (1976). Fig. 2 shows the relationship between SiO_2 and K_2O; from the plot it is apparent that the sampled volcanites can be classified as dacites and rhyolites which, according to their K_2O content belong to two different volcanic suites, the island-arc tholeiitic and the calc-alkaline. Even though this paper is not aimed at discussing the petrochemistry, it is a matter of fact that the classification and the nomenclature herein adopted are in fair accordance with the determined major and trace-element abundances. In particular this applays to the rocks which fall in the calc-alkaline domain, apart from sample TB-11 which displays a K_2O/Na_2O ratio by far higher than 1 and, consequently, quite anomalous for the calc-alkaline series.

Results for radiometric age determinations are reported in table 1 and show that acid volcanites from eastern Pontids exhibit ages ranging from 100 to 24 m.y. Although on statistical basis no age-clusterings are displayed, owing to the limited samples analysed such a feature does not applay to rule out paroxysmal magmatic pulses which likely occurred during tectonic events. K/Ar ages point out that differently K-enriched dacites and rhyolites were emplaced over a wide time-span, i.e. from Cenomanian up to Oligocene times; only one sample, however, yielded Oligocene age.

Besides contributing to implement an absolute time-scale these data represent a tool to shed some light about the chemical evolution of Pontic magmatism, for which two conflicting hypotheses were expressed. In fact, according to EGIN et al. (1979) and BERGOUGNAN and FOURQUIN (1980) the volcanic activity started with emplacement of tholeiitic products and, with time, produced calc-alkaline volcanites; such as important compositional variation is accounted for by two volcanic cycles quite distinct as regards the age of their respective occurrence. MANETTI et al. (1983), in turn, do not agree with the above interpretation and report many evidences which rule out any relationship between emplacement age and chemical affinity of the volcanites. As the latter AA. recognized both calc-alkaline and shoshonitic volcanic associations of Cretaceous age, they claimed that Cretaceous volcanic cycle was notably evolved in Eocene times, when a distinct and unrelated calc-alkaline cycle started. Such an abrupt change in chemical characters was explained in terms of southward motion of the subduction zone and/or slope decreasing of the Benioff zone, since both these mechanisms can determine K-deplete magmatism.

The most interesting information provided by geochronological data is that the ages found do not show any correlation with the K-content of the volcanites, this suggesting that in eastern Pontids acid rocks with different chemical characters were erupted almost simultaneously. The reported occurrence of feldspatoid-bearing volcanites in the Trabzon area further complicates the overall picture, as these latter rocks yielded ages ranging from 67 to 74 m.y. (GUMUS, 1978), thus mostly of the same time-span in which tholeiitic and calc-alkaline acid rocks were emplaced.

TABLE 2

*Silica, age, Rb and Sr contents, 1/Sr*E3, $^{87}Sr/^{86}Sr$ ratios*

Sample	SiO2	age	Rb	Sr	87Rb/86Sr	1/Sr	87Sr/86SrM	87SR/86SrI
TB-38	64.3	45	25	100	.72	10	.70565+2	.70519
TB-11	66.8	95	26	6.9	11.1	147	.72720+2	.71228
TB-28	68.0	101	3	120	.07	8	.70622+2	.70621
TB-14	68.9	63	42	160	.76	6	.70539+2	.70472
TB-56	69.7	75	14	110	.37	9	.70532+2	.70492
TB-25	70.0	49	23	140	.48	7	.70577+2	.70543
TB-60	73.6	24	33	20	4.78	50	.70543+2	.70380
TB-62	73.7	68	12	76	.46	13	.70500+2	.70455
TB-64	75.5	91	28	44	1.84	23	.70760+2	.70522
TB-42	76.7	74	15	51	.85	20	.70553+2	.70464

M = measured values; I = initial calculated values.

Results for $^{87}Sr/^{86}Sr$ ratios, which were measured on the same specimens used to perform K/Ar chronology, are given in table 2. $(^{87}Sr/^{86}Sr)_{initial}$ ratios, calculated by using K/Ar age, Rb and Sr content, varies between 0.70380 ± 0.00002 (TB-60) and 0.71228 ± 0.00002 (TB-11). From table 2 it is also apparent that Sr isotopic composition does not correlate neither with age nor silica content, this likely ruling out systematic ^{87}Sr effects directly inherited from source materials as subducted oceanic slabs. Apart from sample TB-60, whose $^{87}Sr/^{86}Sr$ ratio agrees with a deep seated origin for the parental magma, Sr isotopic composition found for all the remaining samples could be accounted for only by distinct and complicated histories of their individual source regions. At present, however, we can hardly support such an hypothesis, as many data with the studied volcanites are lacking.

A second tentative explanation would be a secondary diffusive contamination of the rocks introduced by a liquid or a fluid. The most reasonable process which can account for secondary $^{87}Sr/^{86}Sr$ modification is represented by interaction, to a variable extent, of high in Sr and, ^{87}Sr-enriched fluids (e.g. bicarbonate-rich fluids), with the volcanites. The above hypothesis receives some degree of support as the volcanites from study area

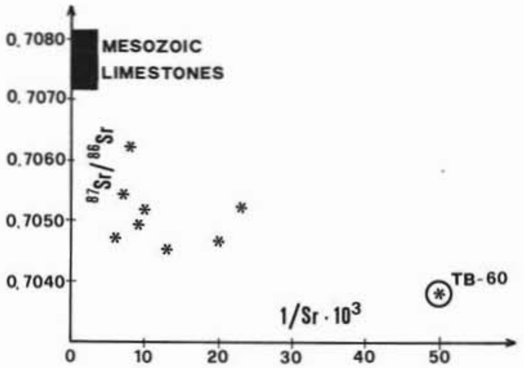

Fig. 3. — ($^{87}Sr/^{86}Sr)_{initial}$ vs. 1/Sr · 1000 relationship for the analysed rocks. Sample TB-11, which is not reported in the graph, is discussed in the text. The dark area in the upper left side of the graph is representative for marine carbonate-bearing rocks.

often contain disseminated sulphide-minerals as well as calcite hydrothermal in origin. In this view it can be supposed that mineralizing fluids upwelling through the fault system likely interacted with the carbonate rocks interbedded within the volcano-sedimentary complex. Consequently, through such a mechanism a $^{87}Sr/^{86}Sr$ ratio comparable to that of Mesozoic limestones occurring in the area ($^{87}Sr/^{86}Sr$ ranging from 0.707 to 0.708, according to VEIZER and COMPSTON, 1974) could be produced. On the other hand, important effects of rock contamination by a phase very high in ^{87}Sr were pointed out by SPOONER et al. (1974). According to these AA., unaltered ophiolitic rocks from Troodos display a mean $^{87}Sr/^{86}Sr$ ratio of 0.7044, while the average ratio increases up to 0.7056 for those samples altered by sea water.

Fig. 3, which shows the relationship between 1/Sr · 1000 and $(^{87}Sr/^{86}Sr)_{initial}$, points out that $^{87}Sr/^{86}Sr$ sympathetically increases with the Sr content. Such a trend gives further support to the hypothesis that volcanics underwent diffusive hydrothermal alteration, likely by mineralizing fluids whose $^{87}Sr/^{86}Sr$ was comparable to that of Mesozoic limestones spread in the Pontids.

Due to different reasons, however, the contamination hypothesis as above suggested is soundless for both sample TB-11 and TB-60. As regards the latter sample, its low $^{87}Sr/^{86}Sr$ would rule out any significative hydrothermal alteration, likely because at the time of its emplacement, dated at 24 m.y., hydrothermal activity was over. On the other hand, sample TB-11, which although ^{87}Sr-enriched is also Sr-depleted, appears to reflect a separate alteration pattern, probably produced by waters related to old salic rocks, that normally display low Sr content coupled with high ^{87}Sr radiogenic.

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