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MAJOR, TRACE ELEMENT AND Sr-Nd ISOTOPE DATA ON NEOGENE ANDESITIC ROCKS FROM THE PIENINY KLIPPEN BELT (SOUTHERN POLAND) AND GEODYNAMIC INFERENCES

Abstract: The andesitic rocks from Mt Wżar and Malinów display low εNd values (-7 to -10) combined with low $^{87}Sr/^{86}Sr$ (ca. 0.7055), showing that their source reservoir was strongly enriched in Nd with regard to Sm on a time-integrated basis, but evolved with a relatively low Rb/Sr ratio. These characteristics depart from those typical of orogenic andesites produced above actively subducting oceanic lithosphere. It is inferred that the limited volumes of magmas emplaced along the PKB were produced by partial melting of enriched mafic lithologies in the lower crust and/or enriched domains in the mantle, probably as a result of local decompression in a broadly transpressive geodynamic setting.

Keywords: Carpathians, Pieniny, tectonics, andesites, geochemistry, Sr-Nd isotopes

TECTONIC SETTING

The Pieniny Klippen belt (PKB) is a long, narrow, highly deformed zone separating the tectonically unlike Inner and Outer Carpathians at the northern flank of this orogen. The PKB extends from Austria, through Slovakia and Poland to Ukraine and includes a variety of tectonically juxtaposed Mesozoic sedimentary successions of diverse palaeogeographical affinities and their thick, synorogenic, Senonian-Palaeogene cover. Steep to vertical dips of the sedimentary strata within the PKB, together with its general megaboudinage-like structure, reflect the prolonged and complex deformation history of the belt, including (1) end Cretaceous folding and thrust-stacking at the front of the Inner Carpathian accretionary complex; (2) Miocene refolding in a transpressional regime together with the Outer Carpathian flysch belt and (3) Miocene to Pliocene sinistral strike-slip of a considerable magnitude (cf. Birkenmajer 1986, Royden 1988, Kováč et al. 1998, Kováč & Plašienka 2002). The latter strike-slip motion may have been associated with a SW- to W-ward subduction of the presumed oceanic crust which occurred in the area of the present-day Inner Carpathians. It also reflected the eastward tectonic escape of the Inner Carpathian (Alcapa block) units towards the remnants of the Tethys ocean due to Africa-Europe collision across the Alpine orogenic belt (e.g. Royden 1988, Nemčok 1993, Kováč et al. 1998).

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Table 1 - Major (wt%) and trace element (μg g-1) concentrations measured by ICP--AES and ICP--MS, respectively, at SARM (CRPG) Nancy. Localities: Wż – Mt. Wżar, Mal – Malinów

Samp.	Wż1	Wż2	Wż3	Wż4	Wż5	Mal
SiO_2	54.6	54.1	53.8	51.2	50.1	58.9
Al_2O_3	18.7	18.7	19.2	18.1	17.8	18.3
Fe_2O_3	7.11	7.13	7.39	8.27	8.01	5.08
MgO	2.89	3.14	3.06	4.52	4.73	1.22
CaO	8.10	8.07	8.14	9.36	8.77	6.68
Na_2O	3.73	3.77	3.89	3.40	3.12	4.05
K_2O	1.65	1.67	1.67	1.80	1.60	1.43
TiO_2	0.69	0.70	0.73	0.83	0.79	0.50
MnO	0.14	0.15	0.13	0.13	0.14	0.13
P_2O_5	0.32	0.32	0.32	0.26	0.28	0.24
LOI	2.01	1.41	1.64	2.07	4.57	3.17
TOT.	99.9	99.2	99.9	99.9	99.9	99.7
Ba	601	598	582	442	512	802
Rb	53.5	52.6	50.1	59.4	51.4	58.2
Sr	606	608	615	593	511	883
Zr	127	128	123	119	112	169
Nb	11.5	11.4	10.0	7.00	6.73	13.3
Ta	0.93	0.89	0.75	0.57	0.55	1.03
Y	18.5	18.7	19.0	20.1	17.7	15.3
Th	5.76	5.96	5.19	5.92	4.11	6.46
U	1.37	1.44	1.54	1.56	1.18	2.23
La	27.7	27.3	23.6	25.2	20.7	32.7
Ce	51.4	51.5	43.6	45.2	39.5	59.0
Pr	5.88	5.81	5.12	5.39	4.60	6.64
Nd	21.5	22.5	20.8	20.8	18.4	25.8
Sm	4.12	4.19	3.90	4.11	3.72	4.34
Eu	1.29	1.39	1.26	1.28	1.18	1.52
Gd	3.59	3.76	3.64	4.10	3.50	3.45
Tb	0.52	0.54	0.56	0.57	0.51	0.51
Dy	3.02	3.26	3.01	3.47	2.97	2.83
Er	1.72	1.69	1.68	1.78	1.50	1.42
Yb	1.80	1.81	1.77	1.85	1.56	1.56
Lu	0.28	0.27	0.28	0.28	0.28	0.27

The several small andesitic hypabyssal intrusions known from the Polish part of the PKB are but an insignificant reflection of the abundant volcanism active in Neogene to Quaternary times over vast areas of the Inner Carpathians, which is widely believed to reflect successive stages of the Cenozoic oceanic crust subduction (e.g. Peckay et al. 1995, Lexa, Konečny 1998) and the subduction hinge roll-back-driven formation of the Pannonian back-arc basin (e.g. Royden 1988). On the basis of spatial distribution, relationship to regional tectonic phenomena, and the chemical composition of lavas, Lexa & Konečny (1998) and Peckay et al. (2004) distinguish four successive (though regionally diachronous) stages of volcanism in the Inner Carpathians: (1) areally distributed felsic calc-alkaline volcanic suite related to initial stages of the back-arc extension, (2) areally distributed intermediate calc-alcaline volcanic suite associated with advanced back-arc extension, (3) "arc-type" andesites related, though in a complex way, to subduction processes and (4) alkali basaltic magmatism reflecting post-convergence extension. Stages (1+2), (3) and (4) are roughly dated at 20-11 Ma, 16-9 Ma and 14-0 Ma, respectively.

Calc-alkaline andesitic intrusions in the Slovakian parts of the PKB, considered to be arc-type rocks (Lexa, Konečny 1998), were dated at 13-11 Ma (Peckay et al. 2004) whereas those in the Polish part yielded K-Ar ages of 22.6 to 10.9 Ma (in particular, two generations of andesite dykes at Mt. Wżar were dated at 14.8 to 10.9 Ma; Birkenmajer, Pécskay 1999).

GEOCHEMISTRY OF ANDESITES

Five samples from the Mt Wżar intrusives (for geological information see Youssef 1978) and one sample from the Malinów quarry have been analysed for major, trace elements and Sr, Nd isotopes. The samples range in composition (Tab. 1) from Al-rich basalt (Wżar 4 and 5) through basaltic andesite (Wżar 1, 2, 3) to andesite (Malinów). Compared to broadly coeval lavas from Central and Eastern Slovakia (Bouvier, Pin, unpubl. res.), the PKB rocks are richer in alkalis at a given silica content, and they display higher concentrations of Ba (440-800 ppm) and Sr (500-870 ppm). Their chondrite-normalized incompatible trace element patterns are fairly homogeneous, with a regular decrease from the more incompatible (Rb, Th, U, K, La) to the less incompatible (HREE) elements, and they all display large negative anomalies of Nb, Ta and Ti. The Rb/Sr ratio is fairly constant for the Wżar samples ($^{87}Rb/^{86}Sr$ = 0.24-0.29). The lowest value (0.19) is found in the more evolved (SiO_2=59 wt%) Malinów andesite, suggesting that this sample did not evolve through fractional crystallization from the same parental magma as the Wżar samples. Sr isotope data (Tab. 2), corrected for *in situ* decay of ^{87}Rb assuming an igneous emplacement age of 15 Ma (by virtue of the very low Rb/Sr ratios, the results are fairly insensitive to the uncertainty on the emplacement age), span a limited range from 0.7053 to 0.7057 in all but one sample (Wżar 3: 0.7067). With the exception of Wżar 3 and Malinów, a faint correlation between $^{87}Sr/^{86}Sr$ and SiO_2 concentrations can be noticed, suggesting that AFC processes may have played some minor role at Wżar. However, at a larger scale, the least radiogenic ratios are observed in both the least (Wżar 5) and in the most (Malinów) silica-rich samples, showing that several, heterogeneous parental melts were involved. Sm-Nd isotope data, reported as initial epsilon values, are tightly grouped at Wżar (εNd from -6.6 to -7.2), while the Malinów sample has an even less radiogenic signature (εNd -9.9). These strongy negative εNd values are indicative of magma sources that were markedly enriched in LREE on a time-integrated basis. Interestingly, the Malinów andesite displays both the lowest $^{87}Sr/^{86}Sr$ (indicative of a low time-integrated Rb/Sr ratio) and the lowest εNd (reflecting a high time-integrated Nd/Sm ratio). This rather unusual feature, departing from the classical reverse correlation of Nd and Sr isotopes, is not in line with conventional petrogenetic schemes for orogenic andesites. These models involve parental magmas that were extracted from time-integrated depleted mantle and underwent variable amounts of crustal contamination, either via recycling of subducted sediments in the mantle, or via assimilation during their ascent through the crust, or both. Compared to Slovakian Inner Carpathian calc-alkaline volcanics (including garnet-bearing andesites), the PKB igneous rocks display distinct radiogenic isotope characteristics, specifically much lower εNd values (-7 to -10, versus from -2 to -5 in Slovakia), combined with mostly lower $^{87}Sr/^{86}Sr$ (ca. 0.7055, versus 0.7050-0.7094). Overall, these radiogenic isotope data imply that the source reservoir of the PKB intrusives was strongly enriched in Nd with regard to Sm on a time-integrated basis, as typical of continental crust materials, but evolved with a relatively low Rb/Sr ratio, unlike most continental materials, including sediments

Table 2. Rb-Sr and Sm-Nd radiogenic isotope data for Pieniny andesites from localities Mt. Wżar and quarry Malinów

	Rb	Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	$^{87}Sr/^{86}Sr_{15Ma}$	Sm	Nd	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	εNd_{15Ma}
Wżar1	53.9	614	0.255	0.705790 (13)	0.70574	4.12	21.5	0.1158	0.512264 (7)	- 7.1
Wżar2	53.2	625	0.250	0.705749 (14)	0.70570	4.19	22.5	0.1126	0.512261 (6)	- 7.2
Wżar3	50.2	632	0.236	0.706793 (12)	0.70674	3.90	20.8	0.1133	0.512291 (6)	- 6.6
Wżar4	58.4	592	0.290	0.705604 (12)	0.70554	4.11	20.8	0.1194	0.512281 (9)	- 6.8
Wżar5	50.9	502	0.291	0.705350 (12)	0.70529	3.72	18.4	0.1222	0.512294 (5)	- 6.6
Malinów	55.9	869	0.191	0.705340 (11)	0.70530	4.34	25.8	0.1017	0.512119 (5)	- 9.9

Rb and Sr concentrations ($\mu g\ g^{-1}$) measured by wavelength-dispersive XRF spectrometry at Ecole des Mines d'Alès;
Sm and Nd concentrations ($\mu g\ g^{-1}$) as measured by ICP-MS (Tab. 1).
$^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios measured by TIMS using an upgraded VG54E instrument in dynamic triple collection mode, and corrected for mass fractionation by normalization to $^{86}Sr/^{88}Sr$=0.1194 and $^{146}Nd/^{144}Nd$=0.7219, respectively. Numbers in parentheses next to each measured isotope ratio are standard errors on the mean, quoted at the 95% confidence level, in terms of the last unit cited.
The NIST SRM987 and the La Jolla isotopic standards measured under the same conditions gave $^{87}Sr/^{86}Sr$=0.71024 ± 2 and $^{143}Nd/^{144}Nd$=0.511853 ± 15. Initial epsilon Nd values were calculated with regard to a chondritic reservoir with present-day values of $^{143}Nd/^{144}Nd$=0.512638 and $^{147}Sm/^{144}Nd$=0.1966, and are precise within ± 0.1 unit.

derived from the upper crust. Felsic granulites, strongly depleted in Rb during an ancient metamorphic episode but still retaining fractionated LREE with low Sm/Nd ratio, might provide a suitable source from an isotopic point of view, but partial melting of such lithologies would produce A-type granitoids, not basalts or andesites, and they can therefore be ruled out, based on major element constraints. Amphibolites derived from ancient, LREE-enriched protoliths such as continental tholeiites or calc-alkaline basalts, might represent more suitable protoliths, although ultramafic sources are more likely for samples of broadly basaltic composition.

In any case, it should be emphasized that the Sr-Nd characteristics of the PKB samples depart markedly from those largely observed in typical orogenic andesites produced above actively subducting oceanic lithosphere, including most continental arc settings. Admittedly, a sound petrogenetic scenario cannot be elaborated from such a limited sample set. Nevertheless, based on the available evidence, it is inferred that the PKB andesitic rocks were probably not extracted from a wedge of depleted mantle fluxed by fluids released from a subducted slab of oceanic lithosphere. Rather, it is suggested that the limited volumes of magmas emplaced along the PKB were produced by partial melting of mafic lithologies in the lower crust and/or enriched domains in the shallow upper mantle, probably as a result of local decompression in a broadly transpressive geodynamic setting.

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