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SULPHUR ISOTOPES OF SELECTED HERCYNIAN GRANITIC AND SURROUNDING ROCKS FROM THE WESTERN CARPATHIANS (SLOVAKIA)

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Abstract: A reconnaissance sulphur isotopic study has been carried out on selected Hercynian granites and related rocks to test the applicability of such data in constraining the relative contribution of igneous and sedimentary protoliths to the West-Carpathian granitic rocks. Chemical separation techniques yielded enough sulphide sulphur for analysis in 22 out of 26 selected whole rock samples. In general, more mafic rocks, showing higher whole-rock bulk sulphur content, yielded more sulphide for isotopic analysis than more felsic ones. The $\delta^{34}S$ values obtained range from –0.9 to +5.7 ‰ (average +2.5 ± 2.3 ‰) for granites of S-type affinity, while results for I-type granites are lower, ranging between –2.9 and +2.3 ‰ (average –0.7 ± 1.9 ‰). Medium grade metamorphic rocks (gneisses ± mica schist) in the area gave values between –2.0 to +4.6 ‰ (average +0.8 ± 2.1‰) similar to S-type granites, while basic igneous rocks, and metamorphic rocks of obvious mantle affinity have a narrow span of values between –0.3 and +1.9 ‰ (averaging +0.7 ± 0.9 ‰). Despite the lithological variability implied above, the range of $\delta^{34}S_{(CDT)}$ values measured is rather narrow when compared with other granitic provinces elsewhere. The results presented here for the West-Carpathian granites fit better within a collisional orogenic setting than in a volcanic arc and/or oceanic subduction scenario. Sulphur isotopic results would be more easily explained within the frame of the I-/S-type model, while other data, such as magnetic susceptibility, could both fit the above and the magnetite-/ilmenite-series typology. Despite this, the data obtained could also be explained within a model in which some sulphur is of deep-seated igneous origin, having a distinctive isotopic composition, and some additional sulphur would be derived from the country rock via assimilation processes that resulted in the Central Western Carpathians granitoid rocks.

Key words: Western Carpathians, Hercynian orogeny, sulphur isotopes, granitic rocks, country rocks, granite typology.

Introduction

An important question in granite petrogenesis is whether a granite was derived from an igneous or a sedimentary protolith. Since Read (1948) pointed out that there are "granites and granites", many typologies have been proposed (e.g. Chappell & White 1974; Ishihara 1977; Debon & Le Fort 1983; Pitcher 1983; Pearce et al. 1984; Maniar & Piccoli 1989; Barbarin 1990; among others). There are many tools to explore this query; e.g. field relations, mineralogy and petrology, physical and geochemical parameters. Determinations of radiogenic and stable isotope ratios have become useful for this purpose as well. It was Coleman (1977) and Sasaki & Ishihara (1979) who first recommended the study of sulphur isotopes in granite petrology. Sulphur is an important element to be considered when trying to understand the genesis of an igneous rock due to a unique set of geochemical characteristics. In most igneous rocks, sulphur is present as a trace element, which usually forms discrete S-rich phases — in granites, mostly sulphides, e.g. pyrite, pyrrhotite, chalcopyrite, and scarce sulphates, e.g. anhydrite; although sulphur may also substitute into other phases, e.g. biotite, muscovite, hornblende and apatite. Indeed, sulphur, as a volatile element, is a sensitive indicator of the degree of interaction between the magma and any S-bearing country rocks into which it is intruded, since sulphur is much more susceptible to mobilisation than other commonly used elements and/or isotopic ratios, e.g. REE's, Rb/Sr, Sm/Nd and Pb (Poulson et al. 1991). Sulphur can be studied by stable isotope techniques, which help to provide information about a number of physico-chemical processes that might have taken place. Magmas formed by partial melting of the mantle, and the rocks and fluids that may evolve from them, should have $\delta^{34}S$ values close to their mantle protolith (Ohmoto 1986). If this protolith is homogeneous, their $\delta^{34}S$ values should be close to zero, relative to the reference standard — the troilite from Cañon del Diablo meteorite (CDT). However, actual igneous rocks have variable $\delta^{34}S_{(CDT)}$ values (Coleman 1977; Sasaki & Ishihara 1979; Kubilius 1983 in Ohmoto 1986; Ishihara & Sasaki 1989; Laouar et al. 1990; Poulson et al. 1991; Recio et al. 1991). Since at magmatic temperatures, no significant isotopic fractionation is to be expected among different S-bearing phases, nor as a result of degassing, this was interpreted by Ohmoto (1986) and Ohmoto & Goldhaber (1997) as the result of assimilation of upper crustal rocks by magmas of mantle or lower crustal derivation. The sulphur content of granites and granodiorites frequently exceeds the amount that would be expected purely as a result of the solubility of sulphide sulphur in the pertinent magmas, and this, coupled with the fact that frequently the $\delta^{34}S$ values of sulphides in the granites and their country rocks are very

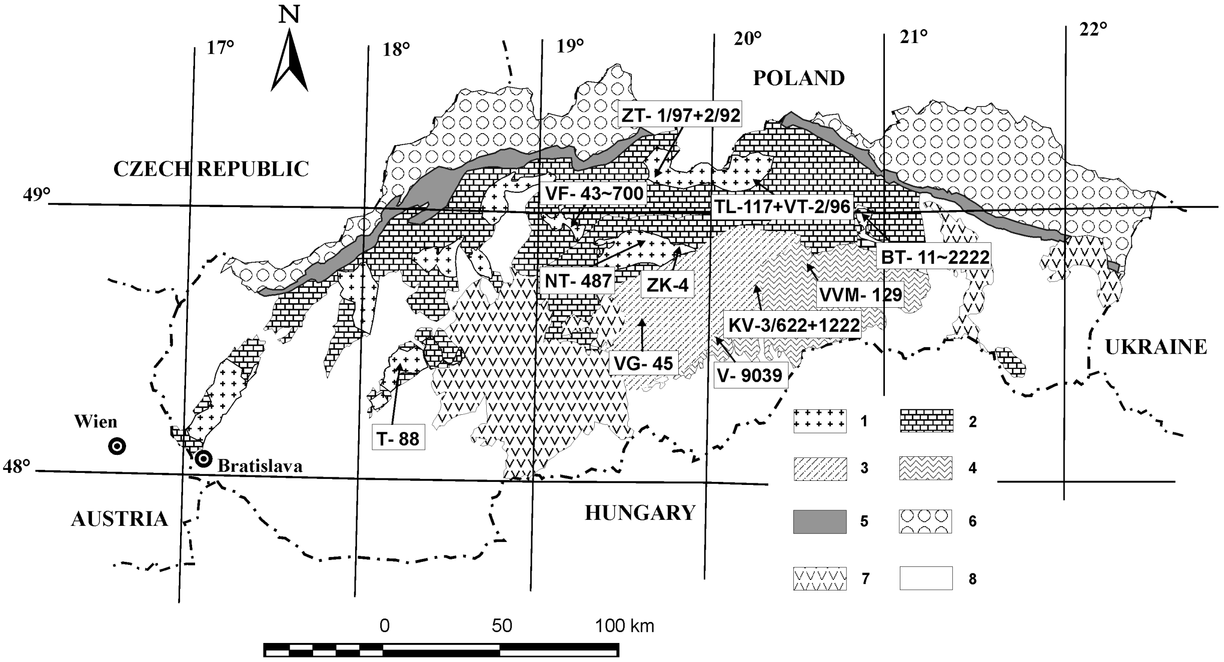

Fig. 1. Simplified tectonic-geological sketch of the Western Carpathians (Slovak part), with location of samples studied. *Explanation of legend:* **1** — Pre-Alpine crystalline basement, Tatric Superunit, **2** — Mesozoic sedimentary cover and nappe structures of the Tatric Superunit, **3** — Veporic Superunit, **4** — Gemeric Superunit, **5** — Klippen Belt, **6** — Flysch zone, **7** — Neogene to Quaternary Central and East Slovak neovulcanites, **8** — Neogene to Quaternary basins. T-88 — Sample locality.

similar, suggests that most of sulphur was actually acquired during granite emplacement. Different sulphur reservoirs have distinctive signatures that might be possible to trace when sulphur becomes part of geological processes, such that well defined patterns of sulphur isotope variations can be identified in granitic rocks (Laouar et al. 1990; Recio et al. 1991).

The purpose of this paper is to report a reconnaissance study on the acid-soluble (monosulphides) and non acid-soluble (disulphides; mostly pyrite) sulphur isotopic characteristics of the Hercynian granitic and surrounding (gabbroic, gneissic, amphibolitic) rocks from the Western Carpathians, for which some preliminary genetic implications have already been discussed by Kohút et al. (2000).

Geological setting

Like the Pyrenees, Alps and/or Himalayas, the Carpathian mountain chain is a typical Alpine collisional fold belt. Its pre-Mesozoic rock complexes, however, belong to the Hercynian basement within the Alpine-Carpathian orogenic belt. During Alpine tectonism, the Carpathian part of the Hercynian belt was disrupted and sliced into blocks, which were incorporated into the Alpine (nappe- and/or terrane-) complexes and subsequently variously uplifted. This polyorogenic history makes reconstructing the Hercynian structures rather difficult, but provides excellent exposures of the various levels of the Hercynian crust. The Western Carpathians form a direct eastern continuation of the Eastern Alps. The pre-Alpine crystalline basement crops out mainly in the Central Western Carpathians (CWC), heart of the Western Carpathians, consisting of three main crustal-scale superunits: the Tatric, Veporic and Gemeric and several cover-nappe systems: the Fatric, Hronic and Silicic (generally from N to S); Plašienka et al. (1997). The Hercynian granitoid rocks occur in all three superunits of the CWC in various positions (Fig. 1). In the Tatric these rocks build backbones of so called core mountains. A large composite granodiorite-tonalite massif, strongly affected by the Alpine tectonics, dominates the Veporic. Another large, hidden granitoid body, penetrating the overlying Early Paleozoic rocks in the form of apophyses, is observed in the Gemeric (Plančár et al. 1977). The core mountains of the Tatric Superunit consist of pre-Mesozoic metamorphic rocks and granitoids, both of which are overlain by Mesozoic cover sediments, and/or nappe structures. Basement rocks were only weakly affected by Alpine metamorphism. The Veporic crystalline basement consists of high- to low-grade metamorphic rocks, various types of granitoids including hybrid ones, and their Upper Paleozoic and Mesozoic cover. As a result of complex Hercynian and Alpine tectonism, this unit has a very complicated — imbricate structure at present. The penetrative brittle-ductile deformation weakens from SE to NW. The basement of the Gemeric is composed of Early Paleozoic (Silurian) to Late Carboniferous, mostly low-grade flyschoid metasediments and metavolcanics, with remnants of an ophiolite complex. This volcano-sedimentary sequence was intruded by small granite apophyses derived from a huge underlying postorogenic body. Granitoid magmatism dominated the Hercynian orogen in the Western Carpathians over a time interval of over 100 million years (360–250 Ma). Accessory mineral associations (magnetite + allanite and monazite + ilmenite) allow distinction of two granite groups (I & S) in the CWC (Broska & Gregor 1992; Petrík & Broska 1994). The occurrence of mafic microgranular enclaves (MME) in the magnetite-bearing granites, and presence of host (metamorphic) rock xenoliths in the magnetite-free granites supports this division. In response to varying geotectonic settings, different genetic types of granites formed: Lower Carboniferous crustal thickening, Upper Carboniferous thermal events, and Permian transtension respectively resulted in S-, I- and A-type granite formation (Petrík & Kohút 1997, and references therein).

Analytical methods

Geochemical analyses (major and minor elements) were done by XRF at the University of Ottawa, and by the classical wet technique at the Geological Survey of the Slovak Republic, Bratislava. The S_{Tot} was measured at the Geological Survey Spišská Nová Ves by ICP–AES. REE were analysed at the Memorial University of Newfoundland, St. John's by ICP-MS (Jenner et al. 1990) and at the MEGA Inc. Stráž pod Ralskem, by INAA. The measurements were verified against natural, international standards (GM and BM from ZGI Berlin). Basic chemical data are presented in Table 1. $^{34}S/^{32}S$ ratios were determined at the Stable Isotope Laboratory of Salamanca University (Spain) on fresh samples, none of which was obviously mineralized. Petrographic examination revealed some minor sulphide minerals, mainly within biotite flakes, occasionally along mica's cleavages as well. Sulphides were also found interstitially between quartz, feldspars and/or hornblende grains, but only sporadically were these observed within these grains. Electron probe microanalysis (EDAX) allowed identification of mainly pyrrhotite and pyrite ± chalcopyrite in the granitic rocks. Additionally, scarce chalcopyrite and sphalerite were identified within surrounding rocks. The generally low sulphur content and small grain sizes prevented physical separation of sulphides. Instead, we have used a chemical extraction technique that is based on the works of Zhabina & Volkov (1978), Canfield et al. (1986) and Hall et al. (1988), but with modifications as described by Recio et al. (1991). This technique uses a digestion apparatus designed by Canfield et al. (1986) to measure the amount of reduced inorganic sulphur in a powdered sample, and the principles described by Hall et al. (1988) for sample preparation for isotopic analysis. Successive use of HCl and $CrCl_2$ on sample weights that varied between 1 and 25 gr. allowed us to separate sulphur (as H_2S) derived from acid soluble sulphides (in this case pyrrhotite; in some samples with very minor sphalerite) from that derived from non-acid soluble sulphides (here mainly pyrite, with a minor contribution of chalcopyrite). During the time to complete the reaction, the evolved H_2S is collected over zinc acetate plus NH_4 solution, and the ZnS produced is converted into Ag_2S by addition of 0.1 M $AgNO_3$. The Ag_2S is preferred for isotopic analysis because it gives higher and more consistent yields during conversion to SO_2 than the ZnS, as well as being more easily recoverable from solution. The yield of clean SO_2 needed for isotopic analysis is prepared by a method similar to that described by Robinson & Kusakabe (1975). The $^{34}S/^{32}S$ ratios were determined in a VG-Isotech SIRA-II™ mass spectrometer. Replicate analyses, including chemistry, of reference standards NBS-123 and NZ-1 (presently referred to as IAEA-S_1) gave an average reproducibility better than ±0.2 ‰. Results are reported in the familiar δ notation, relative to CDT (Cañon del Diablo troilite) in Table 2.

Review of existing data

Despite a long history of application of sulphur isotope data in granite petrogenesis, relatively few $\delta^{34}S$ studies have been carried out when compared with other stable and radiogenic isotopic systems (O, Rb/Sr, Sm/Nd, Pb/Pb). However, from these few studies, a useful pattern emerges. Coleman (1977) has shown that granites from SE Australia (New England Batholith) have sulphur isotope ratios which fall into two groups: those within a small range of $\delta^{34}S_{(CDT)}$ from –3.6‰ to +5.0‰, representing I-type granites in the sense of Chappell & White (1974), and those which are generally higher ($\delta^{34}S_{(CDT)}$ > +5.0 ‰) or lower ($\delta^{34}S_{(CDT)}$ = –9.4 to –3.6 ‰), reflecting S-type granites. The two series of granitic rocks defined by Ishihara (1977) in Japan showed two specific isotope trends in the work of Sasaki & Ishihara (1979). The magnetite-series granites all had positive $\delta^{34}S_{(CDT)}$ values from +1 ‰ to +9 ‰, while the ilmenite-series rocks were dominated by negative $\delta^{34}S_{(CDT)}$ values between –11 ‰ and +1 ‰. In comparison, results from the Sierra Nevada Batholith, as determined by Ishihara & Sasaki (1989), were $\delta^{34}S_{(CDT)}$ from +1.6 ‰ to +4.0 ‰ for magnetite-series granites and from –5.3 ‰ to –3.7 ‰ for ilmenite-series rocks. Two groups, derived from contrasting protoliths, have been identified by Laouar et al. (1990) for the British Caledonian granites. Group I granites (I-type) have $\delta^{34}S$ values within the range –4.5 ‰ to +4.4 ‰, while group II granites (S-type) are strongly positive at $\delta^{34}S_{(CDT)}$ = +6.2 ‰ to +16.0 ‰. Peraluminous S-type granodiorites and granites from the South Mountain Batholith (Nova Scotia) resulted in a wide range of $\delta^{34}S$ values from +1.6 ‰ to +15.0 ‰, indicating that these rocks were influenced by assimilation of the country rocks (Kubilius 1983 in Ohmoto 1986; Poulson et al. 1991). The Proterozoic granitic rocks of Northeastern Brazil, of calc-alkaline and ultrapotassic to shoshonitic affinity, all display positive $\delta^{34}S$ values ranging from +1.0 ‰ to +12.3 ‰ (Sial & Ferreira 1990). Hercynian cordierite-bearing granites of the Central Iberian Zone, Iberian Massif of Spain, have $\delta^{34}S_{(CDT)}$ values from –3.9 ‰ to +4.8 ‰ (Recio et al. 1991). The $\delta^{34}S$ values ranged from +2 ‰ to +9 ‰ for the granitoids hosting porphyry cooper mineralization in Chile, while host rocks of identical mineralization from Philippines gave $\delta^{34}S$ values from –1.4 ‰ to +9.5 ‰, indicating a volcanic arc setting for these magnetite-series rocks and/or deposits (Sasaki et al. 1984). The bulk of data from altered granitic rocks of Bonnet Batholith — Manitoba, with $\delta^{34}S$ values from –1.2 ‰ to +7.5 ‰ (Krouse & Ueda 1987), fall into the range associated with I-type granites, according with Coleman (1977). Cretaceous-Tertiary granitoids of the Kohistan arc — Northern Pakistan, have $\delta^{34}S$ values from –0.6 ‰ to +5.4 ‰, while Cambrian granites of this same arc display higher positive $\delta^{34}S$ from +8.1 ‰ to +9.0 ‰,

Table 1: Chemical composition (major + trace elements and REE) of the studied Carpathian samples. *Explanations:* abT — amphibole-biotite tonalite, mbGD — muscovite-biotite granodiorite, mG — muscovite granite, baD — biotite-amphibole diorite, Gabb — gabbro, b Gn — biotite gneiss, Msch — mica schist, Amph — amphibolite etc. Major elements are in wt. %, trace elements and REE are in ppm.

Sample	VF-43	VF-639	VF-700	TL-117	VT-2/96	ZK-4	VVM-129	VF-356	T-88	VG-45	NT-487	V-9039	KV-3/1222
Type	S-type mbG	S-type bGD	S-type mG	S-type mbGD	S-type bGD	S-type mG	S-type bmG	I-type bT	I-type abT	I-type abT	I-type baD	I/A-type bGD	I/A-type bG
SiO_2	72.66	66.33	73.94	71.24	68.85	73.31	76.09	68.76	66.02	63.66	54.84	69.77	70.31
TiO_2	0.21	0.58	0.16	0.25	0.87	0.08	0.11	0.51	0.75	0.82	1.03	0.38	0.30
Al_2O_3	14.64	15.70	13.27	14.56	14.79	14.07	12.75	15.59	17.00	16.78	14.78	14.05	14.06
Fe_2O_3	0.47	1.62	0.94	1.24	1.18	0.73	0.41	0.81	1.13	1.97	2.01	2.21	1.08
FeO	1.43	1.93	1.25	1.56	2.02	1.35	0.98	2.33	2.89	2.73	5.38	2.06	1.87
MnO	0.03	0.05	0.02	0.04	0.05	0.06	0.03	0.04	0.07	0.06	0.18	0.07	1.16
MgO	0.61	1.21	0.15	0.77	0.96	0.55	0.13	1.22	1.64	2.64	8.32	0.90	0.06
CaO	1.42	2.89	0.69	2.26	2.75	1.10	0.49	2.83	3.36	3.68	5.58	1.53	2.58
Na_2O	3.74	5.01	4.39	4.48	4.33	4.00	2.99	4.04	3.89	3.13	2.67	5.82	3.45
K_2O	3.52	2.94	3.98	1.87	2.47	3.47	4.76	2.24	2.08	2.30	2.63	2.04	4.01
P_2O_5	0.13	0.24	0.21	0.21	0.16	0.16	0.18	0.21	0.20	0.23	0.46	0.11	0.28
H_2O+	0.75	1.24	0.76	1.10	1.10	1.32	0.78	0.94	0.88	1.54	1.88	0.87	0.58
H_2O-	0.18	0.13	0.08	0.18	0.45	0.04	0.11	0.14	0.18	0.21	0.16	0.05	0.25
Total	99.79	99.87	99.84	99.76	99.98	100.24	99.81	99.66	100.09	99.75	99.92	99.86	99.99
S_{tot}	200	320	150	230	320	80	320	220	385	850	800	600	900
Sr	259	365	103	449	565	122	21	563	852	851	680	160	520
Rb	110	91	177	88	108	158	448	91	76	81	102	40	98
Ba	864	641	405	880	821	316	60	826	1015	1021	650	782	848
Zr	112	203	40	159	168	31	66	185	263	249	150	845	159
Y	12.36	11.50	6.36	7.00	13.32	14.99	17.73	6.98	15.18	18.00	16.00	69.00	26.00
Nb	8.79	8.34	6.00	10.00	11.21	9.19	19.65	8.56	12.32	14.00	15.00	40.00	20.00
Ta	0.79	0.44	0.33	0.29	0.40	1.24	5.46	0.62	0.59	0.62	0.25	2.00	0.20
Hf	2.96	4.62	1.21	4.10	4.64	0.91	2.08	4.30	5.32	6.03	4.74	25.90	4.60
Th	6.40	8.90	2.95	6.30	11.23	5.50	9.55	6.26	9.10	12.00	10.20	15.20	28.60
U	2.50	2.20	3.80	2.60	4.50	3.40	6.40	4.10	2.70	3.00	3.50	1.90	9.20
La	20.79	31.20	5.36	26.67	34.77	6.45	7.67	24.56	43.66	86.91	43.95	110.30	73.05
Ce	42.99	66.34	11.04	54.56	71.63	13.40	17.99	51.11	87.90	179.40	96.62	200.30	144.20
Nd	19.73	29.52	4.84	25.67	31.67	5.81	9.51	23.07	38.47	68.79	42.34	106.00	53.84
Sm	4.20	5.41	1.27	3.91	5.98	1.82	2.68	4.17	6.45	10.03	7.28	20.00	9.72
Eu	0.76	1.09	0.42	0.95	1.14	0.45	0.13	1.19	1.58	1.93	1.95	4.83	1.53
Gd	3.32	3.85	1.22	2.89	4.15	2.05	2.20	2.98	4.61	6.07	7.68	-	6.61
Tb	0.47	0.49	0.21	0.36	0.54	0.43	0.48	0.35	0.60	0.70	1.15	2.30	0.90
Tm	0.16	0.15	0.08	0.13	0.18	0.24	0.24	0.08	0.21	0.12	0.35	-	0.43
Yb	0.94	0.95	0.51	0.71	1.03	1.65	1.34	0.51	1.27	0.75	1.95	10.10	2.75
Lu	0.13	0.13	0.07	0.12	0.14	0.24	0.18	0.08	0.19	0.14	0.40	1.67	0.42

although both groups belong to the ilmenite-series (Ishihara et al. 1996). The isotopic composition of sulphidic sulphur from the Žulová massif (NE Bohemian Massif), described by Losos et al. (1994) as a typical ilmenite-series pluton, is relatively homogeneous, with $\delta^{34}S_{(CDT)}$ values ranging from −4.0 ‰ to +3.0 ‰, which are typical values for sulphur derived from deep-seated sources (Hoefs 1997). The sulphur isotope signature of the Hercynian West-Carpathian granites has not been known till present. There were sparse isotopic data from separated sulphide minerals only, from the Cretaceous Rochovce Granite (Repčok et al. 1990), with $\delta^{34}S_{(CDT)}$ values from −0.47 ‰ to +1.88 ‰, documenting an I/A character for this granite. Various poorly identified Hercynian granitic rocks from Central Europe are reported to have a large spread of $\delta^{34}S$ values from −4 ‰ to +12 ‰ (Siewers 1974 in Nielsen 1978).

Unfortunately, little attention has been paid in the literature to the sulphur isotope signature of granite's host-rocks. The sedimentary hosts of some granitic terranes in Japan display strictly negative $\delta^{34}S$ values from −1.4 ‰ to −21.5 ‰ (Sasaki & Ishihara 1979). The metamorphic rocks from the South Mountain Batholith (Nova Scotia) showed a wide range of $\delta^{34}S$ values from −3.7 ‰ to +26.3 ‰, without major differences reported from greenschist to amphibolite facies, or between former pelites and psammites (Poulson et al. 1991). The Dalradian metasediments from Scotland have $\delta^{34}S$ mostly between +11 ‰ and +17 ‰ (Hall et al. 1989). Low-P, high-T metamorphic rocks (nebulites) of the Central Iberian Zone of the Iberian Massif yielded exclusively positive $\delta^{34}S_{(CDT)}$ values between +1.1 and +10.6 ‰ (Recio et al. 1991). It is interesting that greywackes from this area gave both positive and negative $\delta^{34}S$ values of +7 ‰ and around −5 ‰, while intermediate to basic enclaves within the granite were mainly close to 0 ‰, exception made of one quartzdioritic enclave that has a value of $\delta^{34}S$ = +13.4 ‰. Pelitic rocks of the Kohistan arc showed negative $\delta^{34}S$ values from −3.6 ‰ to −7.9 ‰, while metamorphosed pelites have positive $\delta^{34}S$ values from +2.3 ‰ to +10.2 ‰, and amphibolitic rocks reveal $\delta^{34}S$ values from +0.6 ‰ to +3.2 ‰ (Ishihara et al. 1996). High-grade metamorphic rocks of the Ivrea Zone (stronalites and kinzigites; amphibolite- to granulite-facies gneisses) are highly variable, with $\delta^{34}S$ values from −23 ‰ to +13 ‰, typical of marine sediments (Schnetger 1994). Because of the large variation of sulphur isotopic composition, of likely primary sedimentary origin, no difference between groups of metamorphites can be seen. Granulites from Southern Norway also have a large spread of $\delta^{34}S$ from −4 ‰ to +17 ‰, with values around +5 ‰ most frequent (Andreae 1974 in Nielsen 1978). In contrast to

Table 1: *Continued.*

Sample	VF-244	BT-253	BT-217	BT-2222	ZT-1/97	BT-11	ZT-2/92	BT-218	KV-3/622
Type	b Gn	b Gn	b Gn	ab Gn	Msch	Amph	Amph	Gab	Gab
SiO_2	65.07	60.18	65.65	60.67	59.89	58.29	52.65	48.65	48.78
TiO_2	0.76	1.18	0.87	0.47	0.85	0.59	1.08	1.61	0.78
Al_2O_3	16.63	16.39	14.47	15.87	18.82	15.69	14.67	14.43	11.22
Fe_2O_3	2.07	1.82	1.14	1.59	4.25	3.07	4.05	2.40	5.16
FeO	3.95	4.63	4.92	4.65	3.82	3.38	6.69	6.79	6.12
MnO	0.10	0.07	0.10	0.10	0.16	0.11	0.18	0.14	0.16
MgO	1.91	3.24	2.52	3.98	2.21	4.48	6.72	11.62	15.21
CaO	1.31	3.11	1.51	6.06	1.78	6.14	8.84	8.37	7.44
Na_2O	3.20	3.38	2.74	2.94	2.11	3.19	2.74	1.92	1.74
K_2O	3.26	3.27	3.68	1.88	3.98	1.65	0.41	1.69	2.76
P_2O_5	0.26	0.61	0.08	0.10	0.14	0.22	0.17	0.66	0.34
H_2O+	1.27	1.43	1.55	1.07	1.47	2.27	1.11	1.03	0.19
H_2O-	0.12	0.32	0.34	0.29	0.45	0.46	0.21	0.27	0.25
Total	99.91	99.63	99.57	99.67	99.93	99.54	99.52	99.58	100.15
S_{tot}	370	400	450	580	600	750	1150	950	1200
Sr	140	298	199	191	130	130	149	241	638
Rb	139	107	128	61	185	75	22	78	139
Ba	706	1051	564	254	710	284	75	495	635
Zr	190	296	211	100	158	81	82	81	123
Y	23.00	28.00	24.00	13.75	27.00	13.00	19.80	22.00	18.00
Nb	9.00	17.00	11.00	4.75	19.00	4.00	3.85	2.00	4.80
Ta	0.35	0.80	0.90	0.88	1.35	0.70	0.13	1.00	0.50
Hf	4.90	6.00	5.00	2.85	11.00	2.00	1.79	3.00	5.10
Th	15.40	20.00	9.00	6.00	14.00	5.00	0.93	7.00	8.80
U	5.80	5.60	2.10	2.90	4.00	2.30	0.52	2.00	4.00
La	32.94	35.12	35.33	17.63	38.26	13.08	4.45	18.24	55.58
Ce	58.82	71.20	60.46	34.38	75.33	29.11	11.15	41.53	109.70
Nd	32.06	38.34	30.08	15.43	31.92	14.96	7.21	23.07	45.84
Sm	5.70	7.51	5.07	3.23	6.30	3.56	2.32	6.13	9.90
Eu	1.11	1.45	1.10	0.66	1.31	0.65	0.85	1.65	2.05
Gd	4.95	9.82	7.89	3.44	5.36	3.15	3.04	6.65	4.69
Tb	0.65	1.50	1.28	0.61	0.88	0.52	0.55	1.05	0.68
Tm	0.39	0.55	0.60	0.34	0.48	0.25	0.31	0.45	0.27
Yb	2.85	3.05	3.12	1.83	3.08	1.50	2.18	2.38	1.40
Lu	0.41	0.45	0.48	0.27	0.51	0.22	0.32	0.36	0.19

Table 2: Magnetic susceptibility and sulphur isotopic ratio — $\delta^{34}S_{(CDT)}$ values of the CWC samples. M_1 and M_2 represent milligrams of Ag_2S obtained per gram of whole rocks sample reacted (1 mg = 1000 ppm). M_T is the total amount of Ag_2S obtained (from acid-soluble and non acid-soluble fractions). The total $\delta^{34}S$ is the bulk sulphur isotopic value as calculated by mass balance. When only "Total" values are reported, it indicates that no separation between acid-soluble and non acid-soluble fractions was possible (i.e., the sulphide fraction is overly dominated by disulphides), and only the bulk isotopic value for the sample is given.

Sample	Rock type	Magn.susc.	Acid soluble		Non-acid soluble		Total	
		κ (SI u.×10^{-6})	M_1 (mg/g)	$\delta^{34}S$ (‰)	M_2 (mg/g)	$\delta^{34}S$ (‰)	M_T (mg/g)	$\delta^{34}S$ (‰)
VF-43	S-t	181.3					0.015	**-0.95**
VF-639	S-t	1051.0					0.026	**0.56**
VF-700	S-t	0.5					0.010	**1.85**
TL-117	S-t	890.5					0.010	**3.37**
VT-2/96	S-t	2154.0	0.043	0.64	0.052	4.13	0.095	**2.55**
ZK-4	S-t	0.5					0.144	**5.70**
VVM-129	S-t	57.9					0.053	**4.48**
VF-356	I-t	3051.0					0.147	**-1.50**
T-88	I-t	4580.0					0.084	**-2.86**
VG-45	I-t	4509.0	0.024	0.13	3.598	2.35	3.622	**2.33**
NT-487	I-t	4695.0					8.909	**0.70**
V-9039	I/A-t	9645.0					0.765	**-0.69**
KV-3/1222	I/A-t	19575.0					3.263	**-2.01**
VF-244	Gn	958.0	0.021	0.19	0.011	0.71	0.032	**0.37**
BT-253	Gn	1245.0	0.041	2.62	0.085	0.57	0.126	**1.24**
BT-217	Gn	467.5	0.009	4.17	0.152	4.63	0.161	**4.60**
BT-2222	Gn	1425.0					4.860	**-0.11**
ZT-1/97	Msch	564.5	0.448	-2.08	2.034	-1.93	2.482	**-1.96**
BT-11	Amph	6960.0	0.018	-0.34	0.362	-0.26	0.380	**-0.26**
ZT-2/92	Amph	11710.0	0.021	0.69	14.889	1.87	14.910	**1.86**
BT-218	Gab	6155.0	0.005	0.11	0.627	0.85	0.632	**0.85**
KV-3/622	Gab	4635.0	0.102	-3.47	6.942	0.36	7.044	**0.31**

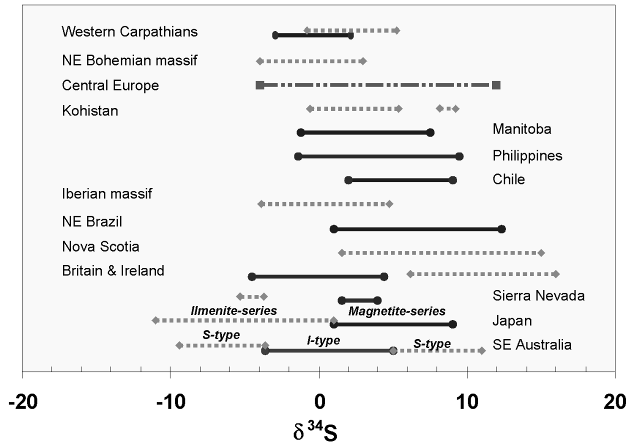

Fig. 2. Ranges of $\delta^{34}S_{(CDT)}$ values for granites worldwide. Sources of data in the text. *Explanations:* Doted line — S-type and/or Ilmenite-series granites. Solid line — I-type and/or Magnetite-series granites. The applicability of this classification to rocks other than those originally used to define it is controversial, however; its use here is for illustrative purposes and does not mean endorsement by the authors. Granites from Central Europe (Siewers 1974 in Nielsen 1978) were not classified by the original author.

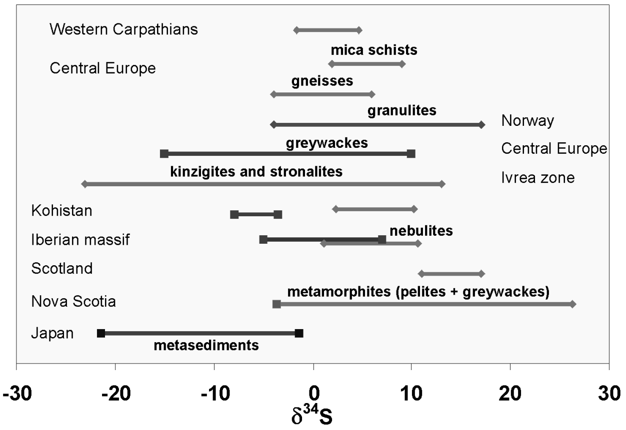

Fig. 3. Summary of $\delta^{34}S_{(CDT)}$ values for the host-rocks of the granitic suites of Fig. 2. Sources of data in the text. *Explanations:* Box — psammite (greywackes) and their metamorphic equivalents. Diamond — pelites and their metamorphic equivalents.

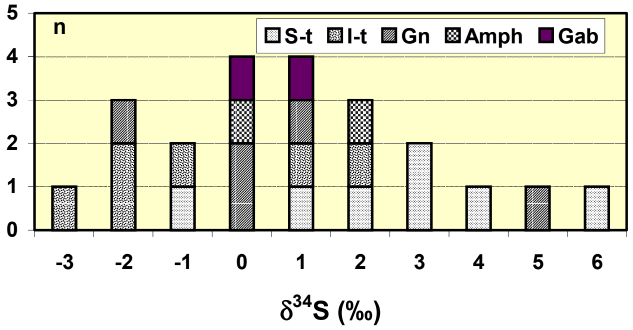

Fig. 4. Histogram of $\delta^{34}S_{(CDT)}$ values from the West-Carpathian rocks. I-t — I-type granites, S-t — S-type granites, Gn — gneisses, Amph — amphibolites, Gab — gabbros.

the above, gneisses from Central Europe have a narrower spread of $\delta^{34}S$ values from −4 ‰ to +6 ‰, while mica schist from the area have positive $\delta^{34}S$ from +2 ‰ to +9 ‰ (Siewers 1974 in Nielsen 1978). In summary (Figs. 2 and 3), no systematic behaviour for the sulphur isotopic characteristics of particular granites and their host-rocks emerges from review of the literature.

Results

Major and trace element contents, including REE, of the studied samples are given in Table 1. Given the limitations of our work, we selected a few samples representative of the whole CWC crystalline basement, focusing mainly on the Hercynian granitic rocks. One sample (KV-3/1222) of the Alpine-Cretaceous Rochovce Granite (Hraško et al. 1999; Poller et al. 2001) is included for comparison. It is obvious from Table 1 that for this research we chose an extremely variegated set of granitoids, from diorite to leucocratic granite, and their host-rocks (represented by gneisses, mica schists, amphibolites and/or gabbro).

The $\delta^{34}S_{(CDT)}$ data of sulphidic sulphur obtained in this work are given in Table 2, and plotted in histogram form in Fig. 4. Chemical separation techniques from whole rock yielded sulphur enough for analysis only in 22 out of the 26 originally selected samples. From Table 2 it can be seen that the sulphur content (expressed as mg Ag_2S per g of whole-rock sample treated) of S-type granites is generally low between 0.010 and 0.144 mg/g (average 0.05 ± 0.05), which is several times lower than sulphur content of I-type granites, that ranges between 0.084 and 8.909 mg/g (average 2.80 ± 3.37). Sulphur content in the gneissic rocks, from 0.032 to 4.860 mg/g (average 1.53±2.13) is within the range of both granite groups. Sulphur content of basic rocks and their metamorphosed analogues (gabbro and amphibolites) is generally high in comparison with felsic crustal rocks. As expected, samples with higher bulk sulphur content (expressed as S_{Tot} in Table 1) yielded more sulphur on chemical treatment for isotopic analysis (Table 2), thus confirming that sulphur-bearing phases are essentially sulphides. Oxidized (I-type; Magnetite-series) granites whose oxygen fugacity is above the NNO buffer may have sulphates; most likely anhydrite, while reduced (S-type, Ilmenite-series) granites carry most of its sulphur in reduced form, as pyrrhotite (Ohmoto 1986; Ohmoto & Goldhaber 1997). A way of testing the reduced/oxidized character of sulphur forms in the rocks under consideration is to plot sulphur content against FeO content. If S is present in reduced form only a positive correlation is to be expected. There is a good correlation between both parameters plotted (Fig. 5), and even I-type rocks plot in trend, suggesting that most sulphur is in a reduced form. Generally distribution of FeO is controlled by presence of biotite within CWC granitic rocks, whereas hornblende is rather scarce in the I-type rocks. Higher content of Fe-Mg silicic minerals is connected with greater amounts of bulk sulphur mainly in the form of minute inclusions within them and vice versa. However, some of the I-type rocks show evidence for additional sulphur phases, most likely oxidized ones, that would have been unaccounted for by our analytical

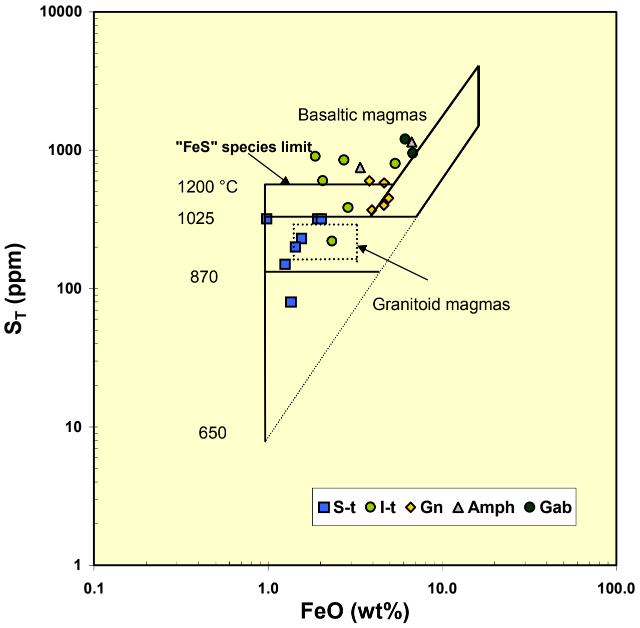

Fig. 5. Plot of total sulphur content versus FeO content according Ohmoto & Goldhaber (1997) for testing the presence of sulphide and sulphate phases in silicate rocks. *Symbols as are marked:* Box — S-type granites, Grey circle — I-type granites, Diamond — gneisses, Triangle — amphibolites, Black circle — gabbros.

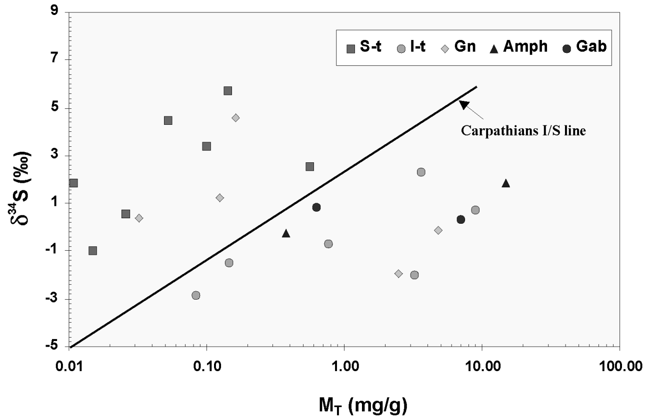

Fig. 6. $\delta^{34}S_{(CDT)}$ values versus sulphur content of samples from the Central Western Carpathians. M_T is yield in mg of Ag_2S (as evolved from total acid-soluble + non acid-soluble sulphides) per g of whole rock sample used. The $\delta^{34}S_{(CDT)}$ value reported is the bulk sulphidic sulphur isotopic composition of the rock as calculated by mass balance, from the results obtained for the acid soluble and non-acid soluble fractions (if available); data from Table 2. Symbols as in Fig. 5.

scheme (that is specific for reduced sulphur; see Canfield et al. 1986; Hall et al. 1988). This should, however, not affect noticeably our main inferences, since according to Ohmoto & Goldhaber (1997; pg. 587) *"... observed isotopic fractionations between sulfate and sulfide from I-type volcanic rocks are in most cases disequilibrium values at magmatic temperatures ... "*. S-type granites, except for one sample, show positive $\delta^{34}S$ values between −0.95 and +5.70 ‰ (average +2.51 ± 2.3 ‰), while I-type granites have $\delta^{34}S$ values in the vicinity of zero, from −2.86 to +2.33 ‰ (average −0.67 ± 1.9 ‰), in good agreement with a possible derivation from lower crustal or mantle sources (Ohmoto 1986). Heavier $\delta^{34}S$ values from −1.96 to +4.60 ‰ (average +0.83 ± 2.1‰) characterize the surrounding medium-grade metamorphic rocks (gneisses ± mica schist), in good agreement with S-type granites. Basic igneous and metamorphic rocks of obvious mantle origin have a narrow span of $\delta^{34}S$ values from −0.26 to +1.86 ‰ (average +0.69 ± 0.9 ‰). However, chemical and petrographical variations within the samples studied are large (Table 1), which contrasts with the rather narrow spread of $\delta^{34}S_{(CDT)}$, and with isotopic values in other granite areas worldwide. Although our research was limited in scope, there is evidently a general overlap of isotopic compositions between both groups of granitic rocks and nearby felsic and mafic rocks (Fig. 4). The sulphur isotopic composition has been plotted against sulphide content of the samples in Fig. 6. S-type granites are characterized by low sulphur content and heavier isotopic values, while I-type rocks are isotopically lighter, but have more sulphur. In terms of sulphur content and isotopic composition, samples plot correctly on each side of the proposed Carpathians I/S line of Fig. 6.

Discussion

Coleman (1977) realized that, in contrast with common belief, S-type granites of the New England Batholith contained higher bulk sulphur that I-types, and used $\delta^{34}S$ values as discriminating criteria, thus introducing sulphur isotopes in granite typology. Considering that the correlation between S_{Tot} as determined by chemical analysis, and Ag_2S content, as determined during sulphur extraction for isotopic analysis is significant ($r = 0.732$, for $n = 22$), we have plotted the sulphur content versus the isotopic values in Fig. 7, and have included Coleman's (1977) divide between I- and S-type granites. Surprisingly, all samples from the CWC, including evidently peraluminous leucogranites and biotite paragneisses, lie within the field for I-type granites in this diagram. However, an I/S line

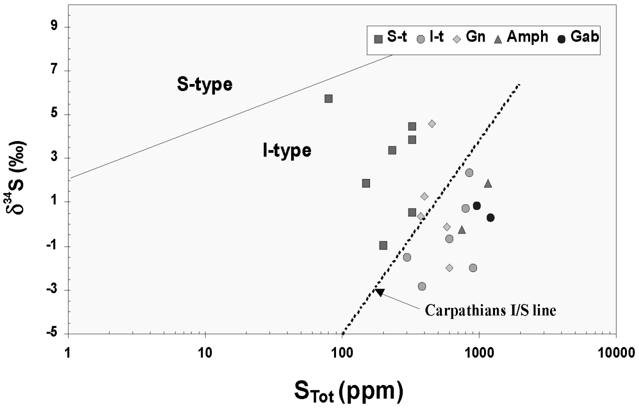

Fig. 7. Plot of $\delta^{34}S_{(CDT)}$ values versus total sulphur content (ppm) for the studied CWC rocks. Solid line dividing S-type and I-type granites is after Coleman (1977); doted line represents the suggested I/S line for the Carpathians granitic rocks. Symbols as in Fig. 5.

for the Carpathian samples can still be drawn. This "Carpathians I/S line" is a better discriminant of supposed sedimentary and/or igneous protoliths of the CWC granitic rocks; indeed, the limited number of metamorphic rocks falls in the correct side of the dividing line. Interestingly enough, when this line is projected onto Sasaki & Ishihara's (1979) Fig. 2, there is better agreement with the Japanese ilmenite-/magnetite-series classification than with Coleman's (1977) I/S dividing line. Hence, we cannot exclude a potentially important contribution of metasedimentary rocks resulting from assimilation (AFC) and/or stoping processes in the genesis of these two main CWC granite groups.

The accessory minerals dichotomy (magnetite + allanite & monazite + ilmenite) of the West-Carpathian granitic rocks (Broska & Gregor 1992; Petrík & Broska 1994) is similar to Japanese granitoids, where Ishihara (1977) defined magnetite- and ilmenite-series granites. The magnetite-series rocks are characterized by magnetite, hematite, ilmenite, and pyrite or chalcopyrite as opaque minerals, while ilmenite-series granitoids are practically devoid of opaque oxide minerals, but contain varying amounts of pyrrhotite in addition to ilmenite. This is in good agreement with observations by Whalen & Chappell (1988), who reported dominantly pyrite in I-type granites, with minor contributions of chalcopyrite and pyrrhotite, whereas S-type granites contained mainly pyrrhotite, with subordinate pyrite and chalcopyrite. Although both classifications share many similarities, it was stated by Takahashi et al. (1980) and Ishihara (1981) that they are not equivalent; the main difference being the tectonic setting; e.g. subduction under a volcanic arc, or collisional thickening, and/or redox state of source-rocks. The ilmenite- and magnetite-series rocks in Japan were well characterized by magnetic susceptibility as well as by their sulphur isotopic ratio (Ishihara 1977; Sasaki & Ishihara 1979). The use of magnetic susceptibility as a petrogenetic parameter has tradition in granite studies in the Western Carpathians (Broska & Gregor 1992; Kohút 1992; Kohút & Janák 1994, among others). The use of Ishihara's value of $\kappa = 3 \times 10^{-3}$ SI units gives good discrimination. Those rocks having $\kappa > 3 \times 10^{-3}$ SI u. are generally considered as magnetite-series rocks (I-type), while granites with lower susceptibility are classified as ilmenite-series (S-type) granites. Since both types of data are available for this work, we have plotted κ versus $\delta^{34}S$ (Fig. 8), following Ishihara & Sasaki (1989), to see how it applies to the CWC rocks. The disagreement in values between West-Carpathian and Japanese rocks is evident. Even when magnetic susceptibility data are in good agreement, $\delta^{34}S$ values are not. The CWC granitic rocks plot all over Ishihara & Sasaki's (1989) diagram, although predominantly in opposite quadrants than granitoid data from Circum-Pacific orogenic belts (Fig. 8). Despite the above, CWC peraluminous leucogranites represent analogues of magnetite-series rocks, while nearly all calc-alkaline biotite (± amphibole–biotite) bearing tonalite can be regarded as ilmenite-series in terms of its sulphur isotopic composition (Sasaki & Ishihara 1979). In spite of the limitations of our data set, it can be envisaged that the misfit of the West-Carpathian Hercynian granitic rocks within the Japanese classification as ilmenite-/magnetite-series rocks may well be related with much different geotectonic setting (subduction under a volcanic arc in Japan, and a continental collisional processes in the Western Carpathians). The most of geochemical features suggest that the CWC granitic rocks are analogous to igneous suites commonly generated by subduction in an Andean-type active continental margin. However, field evidence documents a collisionally thickened crust, with inverted structure of the CWC basement, intruded by a lensoid (sheet-like) granite body within its upper unit (Janák 1994; Kohút & Janák 1994). P-T conditions in the surrounding metamorphic rocks association indicate either an intracontinental subduction or a collisional setting, involving high-grade metasedimentary and metaigneous rocks at lower- to mid-crustal conditions (Janák 1994; Ludhová & Janák 1999). A similar situation has been described for a classical convergent orogen — the Himalaya (Le Fort 1981; France-Lanord & Le Fort 1988; Harrison et al. 1998). It is generally accepted that the CWC granitic rocks were formed as a result of Hercynotype oblique continental collisional processes (Petrík et al. 1994; Kohút & Janák 1994; Petrík & Kohút 1997 among others). The collision induced melting of a vertically zoned lower crust, consisting of various metapelitic and metaigneous rocks, including an old greenstone belt with tonalitic greywacke gneisses as an important constituent.

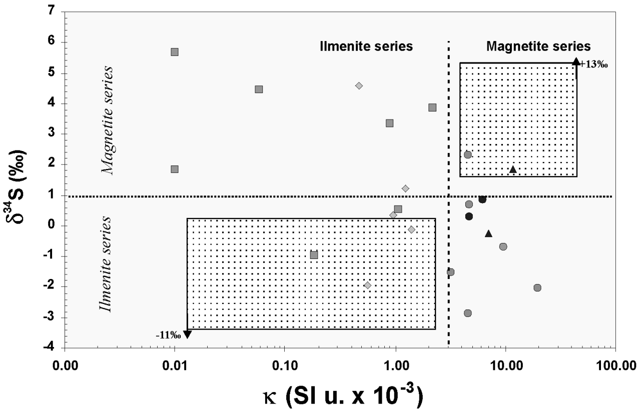

Fig. 8. $\delta^{34}S_{(CDT)}$ versus magnetic susceptibility for the West-Carpathian samples. Doted areas are the fields of "true" Magnetite- and Ilmenite-series granitoids from the Circum-Pacific orogenic belts, according to Ishihara & Sasaki (1989). Symbols as in Fig. 5.

As already mentioned, there are no major differences in sulphur isotopic compositions between arc- and collision-related granitic rocks (Fig. 2). Similarly, there are no big differences between psammitic and pelitic rocks and/or their metamorphic equivalents within these two tectonic settings (Fig. 3). However, in both cases contamination of granitic magmas by partial melting of surrounding, mainly sedimentary, rocks has been widely reported (see for example Ugidos 1990). Assimilation of country rocks is a common process operating during magmatic and final solidification stages of granitic rocks, and can significantly modify granite composition. The incorporation of sedimentary material into the granitic magmas could have been a major reason leading to the reduced character of these granitic rocks. In fact, interaction with pelitic rocks with a high sedimentary organic carbon content can change the character of an originally oxidised, I-type, granitic magma to an ilmenite-series like, reduced, S-type, magma (Ishihara & Sasaki 1989). Similarly, magmas may increase their ore-forming potential by acquiring excess sulphur from the country rocks during emplacement in the upper crust. There are several mechanisms through which the magmas, or an igneous rock, can gain country-rock sulphur, e.g. a) bulk assimilation of volatile and non-volatile elements transfer from country-rocks to magma, b) selective assimilation of country–rock, volatilized, sulphides by the magma, and c) subsolidus transfer via fluids that circulated through the country-rock and the igneous rock (Ohmoto & Goldhaber 1997). Peraluminous, S-type granitic rocks are generally inferred to be produced by crustal anatexis of clastic sedimentary material, such as shales or greywackes, while calc-alkaline, I-type granites are commonly generated by melting of an old (meta)igneous, lower crustal protolith. Recycled crustal sedimentary material is characterized by variable $\delta^{34}S_{(CDT)}$ values from –50 ‰ to +20 ‰, in marked contrast with homogenized lower crustal sources, having $\delta^{34}S_{(CDT)}$ values around 0 ‰ ±1 ‰ (Ohmoto & Goldhaber 1997). The sulphur isotope data from the Western Carpathians are consistent with a hypothesis according to which magmas generated by partial melting of a protolith producing calc-alkaline I-type granitic rocks, encountered protoliths typical of peraluminous S-type rocks at higher crustal levels during ascent within the context of the Hercynian collisional orogeny. Indeed, we cannot ignore the finding that most of sulphur in granitic rocks was actually acquired during their emplacement (Ohmoto 1986; Recio et al. 1991; Poulson et al. 1991), and this fact can partly explain the general similarity of isotopic compositions for both groups of granitic rocks, with narrow spreads of $\delta^{34}S_{(CDT)}$ values, similar to those of surrounding felsic and mafic rocks in the Western Carpathians.

Conclusion

The sulphur isotope study of selected granitic and surrounding rocks from the Western Carpathians reveals that the more basic rocks, having higher whole-rock bulk sulphur contents, yielded more sulphide for isotopic analysis. Our results repeatedly contradict the old opinion that S-type granitic rocks contain greater bulk sulphur than I-type granites. The limited sulphur isotope data-base reveals a relatively narrow spread, when compared with other granite suites worldwide, of $\delta^{34}S_{(CDT)}$, ranging from –2.86 ‰ in I-type tonalites to +5.70 ‰ in peraluminous S-type leucogranites. Isotopic values of CWC granitic rocks generally overlap with values from surrounding felsic and mafic rocks, which span from −1.96 ‰ to +4.60 ‰. The isotopic results reported favour an origin for the West-Carpathian Hercynian granitic rocks within a collisional setting, rather than in a volcanic arc. The $\delta^{34}S_{(CDT)}$ values seem to fit better within the frame of the I-/S-type classification, rather than within an ilmenite-/magnetite-series type of classification. However, even part of the sulphur may certainly be of igneous derivation, it seems highly plausible that CWC granitic rocks may have been involved in assimilation processes of their upper crustal hosts, which would have contributed additional sulphur.

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References

Barbarin B. 1990: Granitoids: main petrogenetic classifications in relation to origin and tectonic setting. *Geol. J.* 25, 227–238.

Broska I. & Gregor T. 1992: Allanite-magnetite and monazite-ilmenite granitoid series in the Tribeč Mts. In: Vozár J. (Ed): The Paleozoic geodynamic domains of the Western Carpathians, Eastern Alps and Dinarides. *GÚDŠ Bratislava, Spec. Vol. IGCP 276*, Bratislava, 25–36.

Chappell B.W. & White A.J.R. 1974: Two contrasting granite types. *Pacif. Geol. (Tokyo)* 8, 173–174.

Canfield D.E., Raiswell R., Westrich J.T., Reaves C.M. & Berner R.A. 1986: The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chem. Geol.* 54, 149–155.

Coleman M.L. 1977: Sulphur isotopes in petrology. *J. Geol. Soc. (London)* 133, 593–608.

Coleman M.L. 1979: Isotopic analysis of trace sulphur from some S- and I-type granites: Heredity or environment? In: Atherton M.P. & Tarney J. (Eds.): Origin of granite batholiths: Geochemical evidence. *Shiva Publishing Ltd.*, 129–133.

Debon F. & Le Fort P. 1983: A chemical-mineralogical classification of common plutonic rocks and associations. *Trans. Roy. Soc. Edinburgh, Earth Sci.* 73, 135–149.

France-Lanord C. & Le Fort P. 1988: Crustal melting and granite genesis during the Himalayan collision orogenesis. *Trans. Roy. Soc. Edinburgh, Earth Sci.*, 79, 183–195.

Hall A.J., Boyce A.J. & Fallick A.E. 1989: A sulphur isotope study of iron sulfides in the Late Precambrian Easdale Slate Formation, Argyll, Scotland. *Mineral. Mag.* 52, 483–490.

Hall G.E.M., Pelchat J.C. & Loop J. 1988: Separation and recovery of various sulphur species in sedimentary rocks for stable sulphur isotopic determination. *Chem. Geol.* 67, 35–45.

Harrison T.M., Grove M., Lovera O.M. & Catlos E.J. 1998: A model for the origin of Himalayan anatexis and inverted metamorphism. *J. Geophys. Res.* 103, 27017–27032.

Hoefs J. 1997: Stable isotope geochemistry. 4th edition. *Springer Verlag*, 1–201.

Hraško Ľ., Határ J., Huhma H., Mäntäri I., Michalko J. & Vaasjoki M. 1999: U/Pb zircon dating of the Upper Cretaceous granite (Rochovce type) in the Western Carpathians. *Krystalinikum* 25, 163–171.

Ishihara S. 1977: The magnetite-series and ilmenite-series granitic rocks. *Mineral. Geol. (Tokyo)* 27, 293–305.

Ishihara S. 1981: The granitoid series and mineralization. *Econ. Geol.* 75th Anniv. Vol., 458–484.

Ishihara S. & Sasaki A. 1989: Sulphur isotopic ratios of the magnetite-series and ilmenite-series granitoids of the Sierra Nevada batholith — A reconnaissance study. *Geology* 17, 788–791.

Ishihara S., Kausar A.B. & Karim T. 1996: Sulphur isotopic profile and granitoid series in the Northern Pakistan. *Proc. Geosci. Colloq., Geoscience Lab, GSP* 15, 57–68.

Janák M. 1994: Variscan uplift of the crystalline basement Tatra Mts., Central Western Carpathians: Evidence from $^{40}Ar/^{39}Ar$ laser probe dating of biotite and P-T-t paths. *Geol. Carpathica* 45, 5, 293–300.

Jenner G.A., Longerich H.P., Jackson S.E. & Fryer B.J. 1990: ICP-MS — a powerful new tool for high precision trace element analysis in the earth sciences: evidence from analysis of selected USGS standards. *Chem. Geol.* 83, 133–148.

Kohút M., 1992: The Veľká Fatra granitoid pluton — an example of a Variscan zoned body in the Western Carpathians. In: Vozár J. (Ed): The Paleozoic geodynamic domains of the Western Carpathians, Eastern Alps and Dinarides. *GÚDŠ Bratislava, Spec. Vol. IGCP Project No. 276*, Bratislava, 79–92.

Kohút M. & Janák M. 1994: Granitoids of the Tatra Mts., Western Carpathians: Field relations and petrogenetic implications. *Geol. Carpathica* 45, 5, 301–311.

Kohút M., Nabelek P.I. & Recio C. 2000: A stable isotope study (O, S) and genesis of the Hercynian granitic rocks from the Western Carpathians. *Abstract Magurka '2000*, Bratislava, 18.

Krouse H.R. & Ueda A. 1987: Contents and sulphur isotope composition of trace sulphate and sulphide in various rock types. *Applied Geoch.* 2, 127–131.

Laouar R., Boyce A.J., Fallick A.E. & Leake A.E. 1990: A sulphur isotope study on selected Caledonian granites of British and Ireland. *Geol. J.* 25, 259–369.

Le Fort P. 1981: Manaslu leucogranite: a collision signature of the Himalaya. A model for its genesis and emplacement. *J. Geophys. Res.* 86, B11, 10 545–10 568.

Losos Z., Hladíková J. & Fojt B. 1994: Mineralogy, trace element and sulphur isotope — geochemistry of sulphide mineralizations related to Hercynian plutonism in the NE margin of the Bohemian massif (Czech Republic). In: Seltman R., Kämpf H. & Möller P. (Eds): Metallogeny of collisional orogens. *Czech Geol. Survey*, Prague, 350–356.

Ludhová L. & Janák M. 1999: Phase relations and P-T path of cordierite-bearing migmatites, Western Tatra Mountains, Western Carpathians. *Geol. Carpathica* 50, 4, 283–293.

Maniar P.D. & Piccolli P.M. 1989: Tectonic discrimination of granitoide. *Geol. Soc. Amer. Bull.* 101, 5, 635–643.

Nielsen H. 1978: Sulfur isotopes in nature. In: Wedepohl K.H. (Ed.): Handbook of geochemistry. *Springer Verlag,* Berlin–Heidelberg, 16-B-1–16-B-40.

Ohmoto H. 1986: Stable isotope geochemistry of ore deposits. In: Valley J.W., Taylor H.P.Jr. & O'Neil J.R. (Eds.): Stable isotopes in high temperature geological processes. *M.S.A. Reviews in Mineralogy*, 16, 491–559.

Ohmoto H. & Goldhaber M.B. 1997: Sulphur and carbon isotopes. In: Barnes H.L. (Ed.): Geochemistry of hydrothermal ore deposits. 3rd edition. *John Wiley & Sons*, New York, 517–611.

Pearce J.A., Harris B.N. & Tindle A.G. 1984: Trace element discrimination diagrams for the tectonic interpretation of granitic rocks. *J. Petrology* 25, 4, 956–983.

Petrík I. & Broska I. 1994: Petrology of two granite types from the Tribeč Mountains, Western Carpathians; an example of allanite (+ magnetite) versus monazite dichotomy. *Geol. J.* 29*,* 59–78.

Petrík I., Broska I. & Uher P. 1994: Evolution of the Western Carpathian granite magmatism: age, source rock, geotectonic setting and relation to the Variscan structure. *Geol. Carpathica* 45, 5, 283–291.

Petrík I. & Kohút M. 1997: The evolution of granitoid magmatism during the Hercynian orogen in the Western Carpathians. In: Grecula P., Hovorka D. & Putiš M. (Eds): Geological evolution of the Western Carpathians. *Mineralia Slovaca—Monograph,* 235–252.

Pitcher W.S. 1983: Granite type and tectonic environment. In: Hsu K. (Ed.): Mountain building processes. *Academic Press*, London, 19–40.

Plančár J., Filo M., Šefara J., Snopko L. & Klinec A. 1977: Geophysical and geological interpretation of gravity and magnetic anomalies in the Slovak Ore Mountain. *Západ. Karpaty, Sér. Geol.* 2, 7–144 (in Slovak with English sumary).

Plašienka D., Grecula P., Putiš M., Hovorka D. & Kováč M. 1997: Evolution and structure of the Western Carpathians: an overview. In: Grecula P., Hovorka D. & Putiš M. (Eds.): Geological evolution of the Western Carpathians. *Mineralia Slovaca—Monograph,* 1–24.

Poller U., Uher P., Janák M., Plašienka D. & Kohút M. 2001: Late Cretaceous age of the Rochovce Granite, Western Carpathians, constrained by U/Pb single-zircon dating in combination with cathodoluminescence imaging. *Geol. Carpathica* 52, 1, 41–47.

Poulson S.R., Kubilius W.P. & Ohmoto H. 1991: Geochemical behaviour of sulphur in granitoids during intrusion of the South Mountain Batholith, Nova Scotia, Canada. *Geochim. Cosmochim. Acta* 55, 3809–3830.

Read H.H. 1948: Granites and granites. *Geol. Soc. Am. Mem.* 28, 1–19.

Recio C., Fallick A.E. & Ugidos J.M. 1991: Sulphur isotope systematics of granitoids and associated rocks from the Avila–La Alberca area (Western Sistema Central, Spain). *Rev. Soc. Geol. España* 4, 371–381.

Repčok I., Eliáš K., Rúčka I., Ferenčíková E., Hašková A., Kovářová A. & Sládková A. 1990: The isotope study of Mo-W ore mineralization near Rochovce. *Open file report, Archive GÚDŠ*, Bratislava, 1–50 (in Slovak).

Robinson B.W. & Kusakabe M. 1975: Quantitative preparation of sufur dioxide for ^{34}S/^{32}S analyses from sulfides by combustion with cuprous oxide. *Anal. Chem.* 47, 1179–1181.

Sasaki A. & Ishihara S. 1979: Sulfur isotopic composition of the magnetite-series and ilmenite-series granitoids in Japan. *Contr. Mineral. Petrology* 68, 107–115.

Sasaki A., Ulriksen C., Sato C.E. & Ishihara S. 1984: Sulphur isotope reconnaissance study of porphyry cooper and Manto-type deposits in Chile and the Philippines. *Bull. Geol. Surv. Japan* 35, 615–622.

Sial A.N. & Ferreira V.P. 1990: Granitoids in northeastern Brazil: Oxygen and sulphur isotope compositions and depths of emplacement. *J. South Amer. Earth Sci.* 3, 1/3, 103–112.

Schnetger B. 1994: Partial melting during the evolution of the amphibolite- to granulite-facies gneisses of the Ivrea Zone, northern Italy. *Chem. Geol.* 113, 71–101.

Takahashi M., Arakami S. & Ishihara S. 1980: Magnetite-series/ilmenite-series vs. I-type/S-type granitoids. In: Ishihara S. & Takenouchi S. (Eds.): Granitic magmatism and related mineralization. *Min. Geol., Spec. Issue* 8, 13–28.

Ugidos J.M. 1990: Granites as a paradigm of genetic processes of granitic rocks: I-types vs S-types. In: Dallmayer R.D. & Martínez García E. (Eds.): Pre-Mesozoic geology of Iberia. *Springer-Verlag*, Berlin, Heidelberg, 189–206.

Whalen J.B. & Chappell B.W. 1988: Opaque mineralogy and mafic mineral chemistry of I- and S-type granites of the Lachland fold belt, southeast Australia. *Amer. Mineralogist* 73, 281–296.

Zhabina N.N. & Volkov I.I. 1978: A method for the determination of various sulfur compounds in sea sediments and rocks. In: Krumbein W.E. (Ed.): Environmental biogeochemistry; methods, metals and assessment. Vol. 3. *Ann Arbor Science Publishers*, 735–745.

Appendix: Sample description and location

Number	rock type location	Latitude	Longitude	Altitude
Sample		(°N)	(°E)	(m)
VF- 43	— muscovite-biotite granite, natural outcrop Vyšná Krivá,	49°01´23″01	19°11´33″20	1035
VF-639	— biotite granodiorite, natural outcrop Blatná valley,	49°00´17″11	19°09´29″40	742
VF-700	— muscovite granite, natural outcrop Nižné Matejkovo,	49°00´09″26	19°15´54″23	825
TL-117	— muscovite-biotite granodiorite, nat.o., Prostredný ridge,	49°11´24″19	20°01´31″23	1920
VT-2/96	— biotite granodiorite, nat.outcrop, Velická valley,	49°09´47″38	20°09´17″44	1925
ZK-4	— muscovite granite, natural outcrop Vyšná Boca,	48°55´28″56	19°44´28″57	1045
VVM-129	— biotite-muscovite granite, drill well Peklisko,	48°48´40″58	20°33´39″49	596
VF-356	— biotite tonalite, quarry Vyšné Matejkovo,	48°59´47″22	19°15´03″59	812
T-88	— amphibole-biotite tonalite, nat.o., Javorový Hill,	48°46´08″05	18°52´30″05	715
VG-45	— amphibole-biotite tonalite, quarry, Kamenistá valley,	48°35´23″11	19°36´59″36	855
NT-487	— amphibole-biotite diorite, natural outcrop, Bôr ridge,	48°58´27″53	19°32´43″48	1715
V-9039	— biotite granodiorite, natural outcrop, Turčok,	48°36´15″10	20°10´08″22	425
KV-3/1222	— biotite granite, drill well Rochovce,	48°42´04″06	20°17´39″21	408
VF-244	— biotite gneiss, natural outcrop, Smrekovica ridge,	48°58´07″55	19°15´01″18	1035
BT-217	— biotite gneiss, natural outcrop, Patria ridge,	49°00´53″30	20°54´03″41	905
BT-253	— biotite gneiss, natural outcrop, Zvoľanská ridge,	49°00´40″32	20°53´12″35	955
BT-2222	— amphibole-biotite gneiss, road tunnel, Svinka valley,	49°00´21″53	20°52´54″05	750
ZT-1/97	— mica schist, natural outcrop, Žiarská valley,	49°09´12″26	19°42´53″38	1015
BT-11	— amphibolite, natural outcrop, Zvoľanská ridge,	49°00´11″21	20°53´57″03	920
ZT-2/92	— amphibolite, natural outcrop, Žiarská valley,	49°09´04″42	19°42´35″18	985
BT-218	— gabbro, natural outcrop, Patria ridge,	49°00´51″53	20°53´57″03	915
KV-3/622	— gabbro, drill well Rochovce.	48°42´04″06	20°17´39″21	408