ZESZYTY NAUKOWE POLITECHNIKI ŚLĄSKIEJ 2005
Seria: GÓRNICTWO z. 268 Nr kol. 1696

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GEOCHEMIA GÓRNOKARBOŃSKICH TONSTEINÓW Z ZAGŁĘBIA WĘGLOWEGO SABERO (NW HISZPANIA)

Streszczenie. Przeprowadzono wstępną charakterystykę geochemiczną tonsteinów w basenie węglonośnym Sabero (NW Hiszpania). Tonsteiny charakteryzują się średnią do wysokiej zawartością pierwiastków ziem rzadkich, Zn, Li, Y, Sr, Zr, Th i U oraz niską zawartością Sc, V, Cr, Co, Hf, P, Ta Ni, Nb, Ti. Stosunek Th/U jest względnie wysoki. Tonsteiny te cechuje znacząca anomalia negatywna Eu oraz wzbogacenie w LREE względem HREE. Powyższa charakterystyka sugeruje, że źródłem tych tonsteinów była raczej magma o składzie odpowiadającym ryodacytom do ryolitów.

GEOCHEMISTRY OF UPPER CARBONIFEROUS TONSTEINS FROM THE SABERO COALFIELD (NW SPAIN)

Summary. Preliminary geochemical characterization tonsteins has been performed in the Sabero coalfield. Tonsteins in the study area are medium to high concentration in REE, Zn, Li, Y, Sr, Zr, Th and U; whereas, low in concentration Sc, V, Cr, Co, Hf, P,Ta Ni, Nb, Ti and relatively high Th/U ratio as well distinctive Eu anomaly. All this is consistent generally with a silicic magmatic source. Particularly, enrichment of LREE and low content of Hf, Ta, and Ti depletion of indicates rather highly evolved magmas which have incorporated either subcrustal material from the continental plate or subducted sediments high in volatiles. Based on the mentioned data it can be concluded that the Sabero tonsteins were likely derived from a calc-alkaline rhyodacitic to rhyolitic eruptive source.

1. Introduction

Ten different tonstein horizons have been located in the Late Carboniferous coal-bearing sediments of the Sabero Coalfield (Cantabrian Zone, NW Spain) (Fig. 1–2). Petrographic studies (Knight et al. 2000) has revealed that these tonsteins are mainly composed of kaolinite, quartz, feldspars (plagioclases), and accessory minerals: zircon and apatite. The composition and petrographical features are entirely consistent with a pyroclastic origin. They are characterized by wide lateral extents, however relatively thin uniform thickness mostly ranging between 2–5 cm, and sharp contacts with confining strata. The main aim of this work is geochemical characterization of Sabero Coalfield tonsteins.

2. Methods

Tonsteins were crushed and pulverized to obtain homogeneous samples suitable for whole-rock analysis. ICP-MS analyses were performed on fused glass discs using a Perkin-Elmer Elan 6000 quadropule mass spectrometer in Activation Laboratories, Ltd. in Canada.

3. Geological setting

The Sabero coalfiled is located in the south of the Cantabrian Zone (Fig. 1). This area constitutes the external zone of the Variscan orogenic belt in the NW of the Iberian Peninsula.

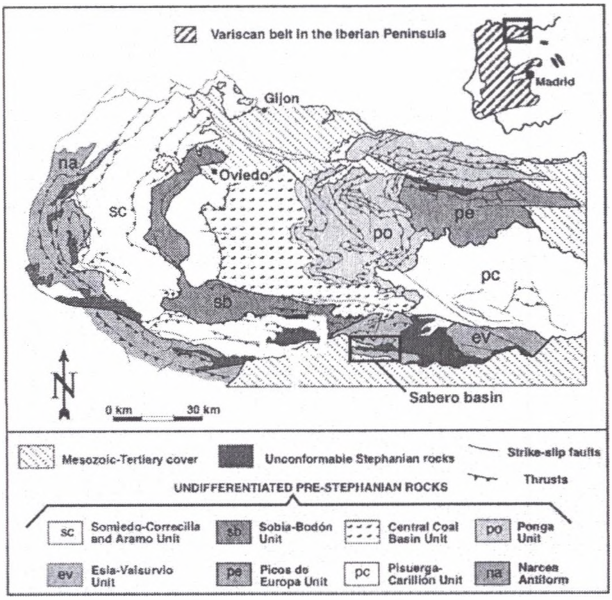

Fig. 1. Geological sketch map of the Cantabrian Zone (after Perez-Estaun et al. 1988). The framed area enclose the Sabero Coal Basin

Rys. 1. Schematyczna mapa geologiczna strefy Kantabryjskiej (Perez-Estaun et al. 1988). Obszar w ramce obejmuje basen węglonośny Sabero

Two different successions can be recognised in relation to the Variscan deformation: one pre-orogenic and one syn-orogenic. The pre-orogenic sequence is formed by Lower Palaeozoic siliciclastic rocks and Devonian carbonate and clastic formations. The syn-orogenic Carboniferous pile (of up to 8 km thickness) is interpreted as a foreland basin sequence (Julivert 1971; Marcos & Pulgar, 1982). Both successions were complexly folded and thrusted under a thin-skinned tectonic regime between Westphalian B and Stephanian times (Julivert 1971, Bastida et al. 1999). The Sabero basin is a pull-apart, intramontane coal basin located along the Sabero-Gordón fault line, one of the major, E-W trending, strike-slip fault systems of the Cantabrian Zone (Colmenero & Prado 1993).

The total thickness of the succession is in excess of 2000 m, and is composed of conglomerates, sandstones, shales and siltstones, with intercalated coal seams with tonsteins.

4. Results and discussion

Over fifty elements (major and trace) were analysed by means an ICP-MS technique in ten different tonstein horizons from Sabero Coalfield (Tab. 1, Fig. 3-5). This study focuses on those trace elements which show apparent differentiation during magmatic evolution, but are relatively immobile during surficial alteration and later diagenesis of volcanic ash to tonsteins in peat-accumulating environments. Immobile trace elements and rare earth elements (REE) have been used to provide information on the magmatic composition of tonsteins parent ashes and tectonic setting of the source volcanoes (e.g. Huff 1983, Kramer et al. 2001, Grevenitz et al. 2003). These studies have generally relied on the use of empirically based discrimination plots derived from studies of igneous rocks of known origin, and while not providing absolute proof of magmatic origin or affinity, these diagrams serve as useful sources of information about the tectonic settings and general magma chemistry, particularly in cases where other geological evidence is ambiguous.

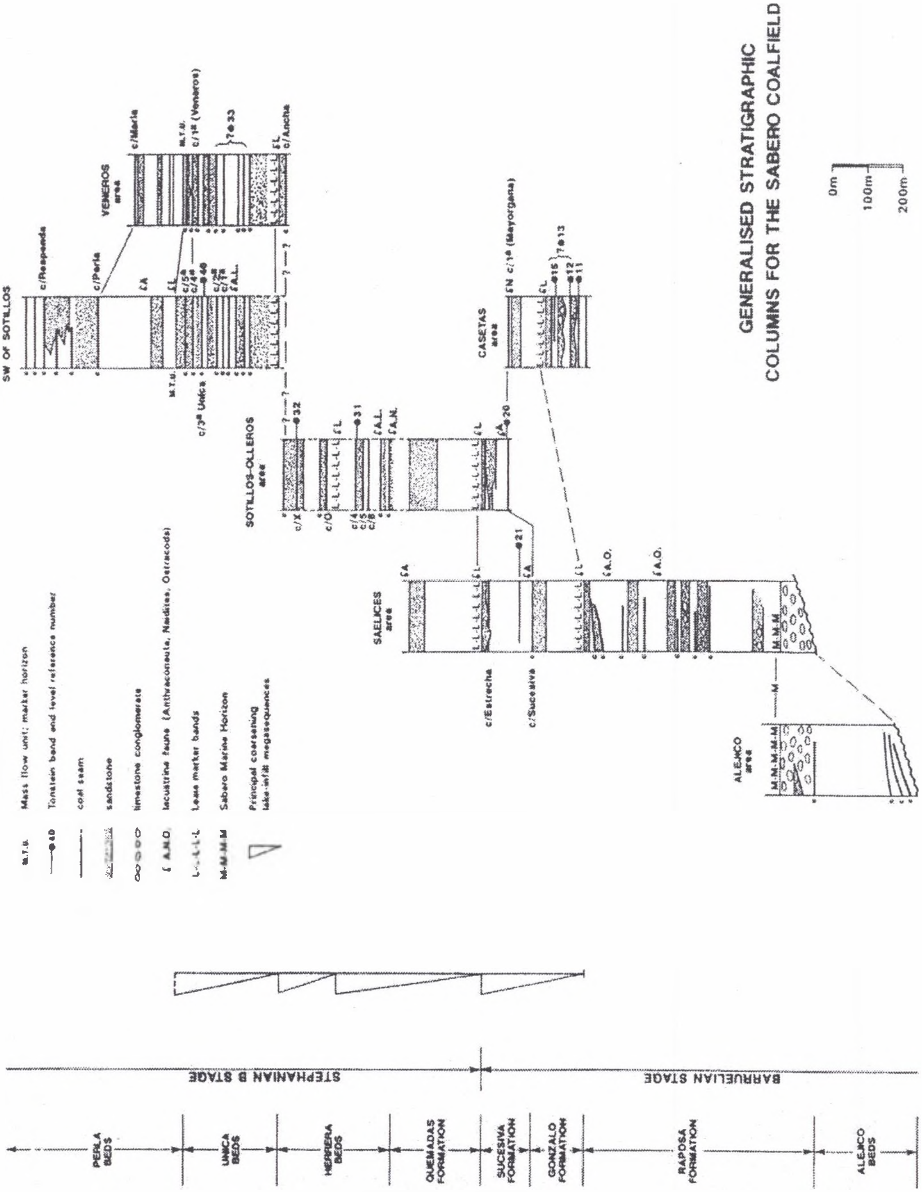

Fig. 2. Lithostratigraphic positions of the tonsteins in the Sabero Coalfield (after Knight et al. 2000)
Rys. 2. Pozycja tonsteinów na tle litostratygrafii basenu Sabero (Knight et al. 2000)

The immobile element composition of Sabero tonsteins, as is characteristic for most tonsteins beds, suggests the source magmas were generally felsic in nature, and thus it is reasonable to employ geochemical discrimination diagrams designed for felsic igneous rocks in assessing their magmatic origins. In Fig. 3 a plot of the immobile elements Rb against Nb and Y shows that almost all samples lie in the field of volcanic arc granite as defined by Pearce et al. (1984), suggesting that some crust components dominate the magma chemistry. One sample lies within the ocean ridge granite field. It may well be that the source volcanics represent the mixing of two or more source magmas in various proportions. It is also possible that upper mantle mafic plumes acted as a heat source for, and made some contribution to, the melting of more felsic rocks in the lower crust. In either case these data argue for a volcanic origin in a subduction-related setting involving the partial melting of continental crust. Whether the source volcanoes were situated as part of a magmatic arc along a plate margin or as arc volcanoes resting on fragments of continental crust and generated as a consequence of plate convergence is unclear. The geochemical evidence, and particularly the discrimination diagrams, suggests only that the magmatic sources were subduction-related and that the melting of some continental crust was involved in their formation.

Studies of the REE patterns in bentonites and tonsteins are useful for distinguishing between samples and estimating original ash compositions. The total rare earth elements (REE), excluding Y for Sabero tonsteins are in the range from 116 to 303 ppm, averaging 210 ppm. Eu/Eu* falls in the range of 0.10–0.35 (Tab. 1). Concerning the ratio Eu/Eu* is calculated concentration based on the values measured for Sm and Gd using methods of Taylor & McLennan (1989). LREE / HREE ratios are in the range of 4–10 (exept of one sample – P85 with value 2) (Tab. 1).

Table 1

Results of geochemical analyses.

All values are in ppm, except of Na, Mg, Al, P, S, K, Ca, Fe in %.

Sample	P121	P142	P22A	P24	P37	P44	P60	P75	P85	P89
	12	32	11	12	40	21	32	20	31	33
Element										
Li	15,97	16,01	33,04	48,64	34,80	35,59	21,64	46,29	66,80	17,32
Be	0,84	2,09	2,03	2,12	1,57	2,39	2,24	2,39	3,06	4,34
Al.	1,38	1,06	1,60	2,31	2,19	2,74	1,49	1,98	4,02	1,33
P	0,03	0,05	0,03	0,09	0,11	0,10	0,04	0,01	1,21	0,12
K	0,09	0,10	0,09	0,18	0,13	0,45	0,07	0,21	0,21	0,06
Ca	0,15	0,21	0,10	0,29	0,44	0,82	0,27	0,14	3,68	0,29
Sc	5,05	2,71	0,27	2,00	3,50	9,80	1,71	1,57	5,49	3,14
Ti	0,01	0,01	0,02	0,01	0,02	0,01	0,01	0,02	0,01	0,01
V	6,42	8,34	3,54	8,72	13,72	12,12	4,97	1,23	8,79	9,77
Cr	6,63	5,31	4,82	9,28	38,62	6,08	5,72	4,82	8,60	19,59
Mn	5,42	68,56	33,91	38,47	96,62	460,36	20,89	23,38	52,47	19,48
Fe	0,24	1,44	0,35	0,45	0,91	4,62	0,10	0,33	0,58	0,71
Co	0,95	7,87	1,61	9,05	7,79	6,80	3,55	1,04	4,42	6,13
Ni	5,17	20,08	4,05	13,11	29,65	8,67	8,50	3,53	10,90	21,39
Cu	6,42	15,39	13,72	22,20	20,07	8,84	15,44	11,86	17,58	15,72
Zn	12,15	128,57	78,73	101,20	109,45	75,68	108,67	54,82	103,22	92,97
Ga	6,67	4,47	4,97	5,48	4,65	8,73	4,67	6,61	11,85	4,46
Se	0,56	1,08	2,26	1,02	1,21	1,20	1,08	0,93	4,24	1,48
Rb	6,84	7,47	4,80	10,74	8,10	21,14	4,20	6,82	13,02	5,04
Sr	80,14	213,09	174,72	93,67	73,34	139,78	105,37	52,82	378,08	910,22
Y	17,03	22,14	35,81	16,96	19,35	23,59	26,45	29,32	112,67	34,06
Zr	4,43	22,15	17,60	0,84	0,55	0,87	27,51	4,86	0,80	30,21
Nb	0,10	0,20	0,14	0,10	0,10	0,10	0,78	0,10	0,10	2,27
Mo	0,19	3,69	0,92	1,79	1,60	0,79	1,82	0,58	2,53	2,97
In	0,13	0,12	0,20	0,11	0,07	0,13	0,08	0,12	0,19	0,15
Sn	1,47	4,51	1,97	1,23	2,01	3,07	4,35	2,40	4,37	6,82
Te	0,03	0,05	0,03	0,04	0,05	0,05	0,04	0,02	0,06	0,05
Cs	0,78	1,77	0,96	1,50	0,85	2,13	0,57	1,14	2,85	0,65
Ba	191,82	48,62	174,87	196,57	114,18	193,89	130,66	204,07	237,04	28,05
La	56,93	39,48	60,99	46,15	24,30	26,49	47,07	21,05	43,41	68,07
Ce	97,79	62,21	108,57	78,58	46,03	50,83	82,48	38,23	76,21	104,80
Pr	14,10	8,85	17,71	11,75	7,44	7,58	11,63	5,96	11,70	15,20
Nd	48,85	30,72	66,62	43,69	29,24	29,97	43,54	22,55	46,28	51,58
Sm	10,97	7,09	15,40	8,89	7,31	7,27	9,59	5,44	14,76	11,65
Eu	0,91	0,45	0,45	0,73	0,80	0,38	0,45	0,20	1,91	0,95
Gd	9,61	6,97	12,43	7,87	6,91	7,33	8,63	5,58	24,03	11,39
Tb	1,28	1,11	1,66	0,90	0,94	1,10	1,16	1,07	4,22	1,78
Dy	5,56	5,65	9,00	4,17	4,75	6,06	6,41	6,73	25,59	9,42
Ho	0,87	1,09	1,77	0,76	0,90	1,13	1,23	1,40	4,90	1,69
Er	2,03	2,70	4,31	1,83	2,20	2,65	3,21	3,87	11,70	4,29
Tm	0,26	0,39	0,63	0,24	0,27	0,37	0,47	0,56	1,42	0,59
Yb	1,49	2,45	3,67	1,33	1,59	2,28	2,99	3,56	7,32	4,00
Lu	0,14	0,31	0,42	0,14	0,19	0,28	0,35	0,43	0,81	0,52
REE	250,80	169,48	303,62	207,01	132,86	143,72	219,21	116,64	274,26	285,92
LREE (L)	228,64	148,35	269,29	189,06	114,31	122,14	194,31	93,23	192,35	251,30
HREE (H)	22,16	21,14	34,33	17,95	18,55	21,59	24,90	23,41	81,91	34,63
(L)/(H)	10,32	7,02	7,84	10,53	6,16	5,66	7,80	3,98	2,35	7,26
Eu/Eu*	0,27	0,20	0,10	0,26	0,34	0,16	0,15	0,11	0,31	0,25
Hf	0,10	0,83	0,58	0,10	0,10	0,10	1,09	0,24	0,10	1,24
Ta	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05
Pb	15,85	39,86	89,59	84,31	80,44	20,18	44,14	77,59	74,75	61,19
Th	34,40	19,73	40,80	27,13	24,74	25,97	32,15	23,48	30,01	28,64
U	6,66	11,29	13,54	2,37	7,18	8,41	10,89	12,48	10,76	15,94

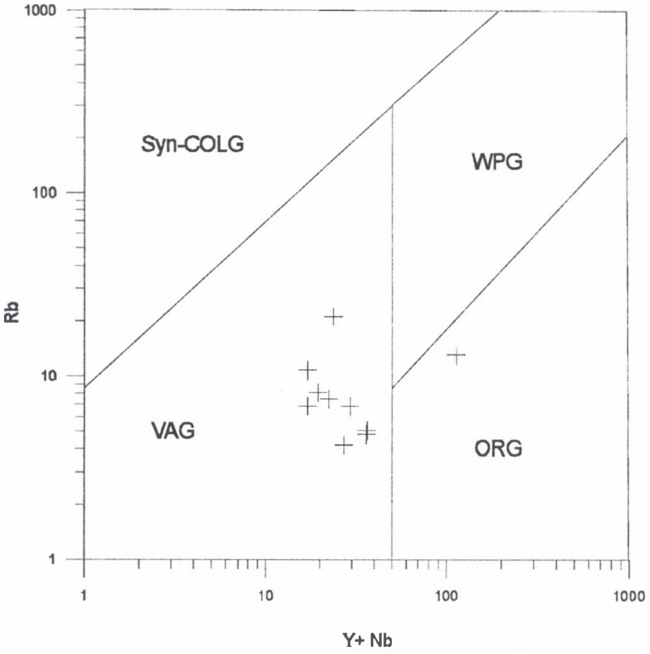

Fig. 3. Tectonic discrimination diagram showing Rb vs. Y+ Nb (after Pearce et al. 1984) for Sabero tonsteins. VAG - volcanic arc granite; ORG - ocean ridge granite; WPG - within plate granite; Syn-COPLG - syn-collisional granite

Rys. 3. Diagram dyskryminacji tektonicznej Rb w stosunku do sumy Y oraz Nb (wg Pearce et al. 1984) dla tonsteinów Sabero. VAG – granity wylkanicznych łuków wyspowych; ORG – granity grzbietów oceanicznych; WPG – granity wewnątrzpłytowe; Syn-COPLG – granity synkolizyjne

REE ratio curves (Fig. 4) have moderate to relatively steep slopes reflecting LREE enrichment. All samples have negatively sloping curves with an overall enrichment of light rare earth elements (LREE) of 100–300 times chondritic, and of heavy rare earth elements (HREE) a factor of 10-20. Both features are characteristic of calc-alkaline magmas erupted in subduction-related volcanic arc environments (Taylor & McLennan 1989). On the Fig. 4 is shown negative Eu anomaly for all Sabero Coalfield tonsteins. The significant negative europium anomalies of sample sets is characteristic of silicic igneous rocks. The presence of such pronounced negative Eu anomaly could suggests earlier crystallization of plagioclase (?) and a bulk composition that is more felsic (Huff 1983).

Sc is a typically immobile element during surficial weathering and alteration. In the organic-rich, low-pH environment of the peat swamp, Sc is easily adsorbed by clay minerals as metallorganic complexes (White 2003). The immobility of Sc during weathering and later diagenesis makes it a reliable indicator of the source chemistry of clay partings in coal. Sc concentrations of Sabero tonsteins are from 0,3 to 9,8 ppm (Tab. 1). The average values in mafic rocks are 24–40 ppm, in intermediate and silicic rocks ~4 ppm and 2–3 ppm in alkaline rocks (White 2003). Analysed tonsteins likely derived from calc-alkaline, low-silica volcanic (P142, P22A, P24, P37, P60, P75, P89) ashes can be discriminated from those derived from more silicic progenitors (P44, P121, P85) (Tab. 1).

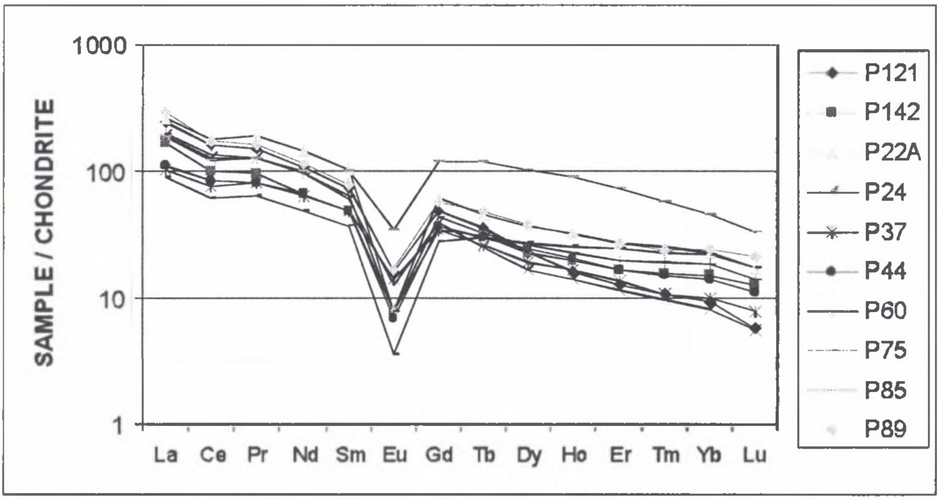

Fig. 4. Rare earth elements (REE) patterns for Sabero Coalfield tonsteins. Chondrite normalising values based on McDonough & Sun (1995)

Rys. 4. Rozkład dystrybucji pierwiastków ziem rzadkich w tonsteinach basenu Sabero

Zr and Hf are very similar in electron configuration and geochemical characteristics. In silicic and mafic rocks, there appears to be no significant difference in Zr and Hf contents or in Zr–Hf ratios. However, Zr and Hf contents increase dramatically in calc-alkaline rocks (White 2003). Both elements are quite immobile in the surficial environment. The data of this study show a positive correlation between Zr and Hf (Fig. 5a). Sabero tonsteins have generally diversified content Zr but relatively low content of Hf.

The concentrations of V and Ti vary dramatically among different types of magma. In the surficial environment, however, their immobility survives the alteration process. The concentrations of these elements in sediments are very close to those of the parent rocks from which these sediments were derived (White 2003). Since Ti has a high resistance to the weathering process, it tends to become enriched in the residual products. However, as shown in the V–Ti scatter diagram (Fig. 5b) Ti concentrations in the Sabero tonsteins is very low (below 0,025 ppm) and V content is from 1,2 to 13,7 ppm.

In mafic rocks, Th and U concentrations average 4 and 1 ppm, while in silicic rocks they average 17 and 3 ppm, respectively (White 2003). Uranium is much more soluble than thorium in oxidizing surficial and ground waters, leading to a larger range of U concentration and, hence, a more variable Th/U value in sediments. In the plot of Th vs. U (Fig. 5c) data of the Sabero tonsteins fall within similar composition ranges characteristic rather for more silicic rocks. Th/U ratio is from 2 to 11, in average quite high 4.

Co and Cr are siderophile elements; their abundance in mafic rocks is an order of magnitude higher than that in silicic rocks (White 2003). Ca-rich, silicic eruptive rocks rhyodacites are low in Co compared to more silicic, K-rich lavas. Both rhyolites and pantellerites i.e., calc-alkalic rhyolites have average Cr concentrations lower than 2 ppm (White 2003). A plot of Co vs. Cr (Fig. 5d) shows that the tonsteins are relatively low in both Co and Cr inherited from their presumed rather silicic source rocks.

Among other elements, Li, Be, Se, and Mo – these elements vary in concentration for Sabero tonsteins from various horizons, probably because they do not remain immobile during extensive weathering and alteration. Therefore, they are much less likely to retain any fingerprint of the original material and are not used here for determination of origin of tonsteins. Whereas, concentration of Ta, Ti and Nb seems to be below detection limit of applied quadropule ICPMS.

The identification of diagnostic trace-elemental signatures and their concentration levels can contribute to the distinctive characterization of individual tonsteins, confirmation of their origin volcanic vs. detrital, and estimation of their source magma composition. Certain elements Al, Ti, W, Be, Sc, Nb, Ta, Zr, Hf, Cr, Co, Th, and REE in acid to nearly neutral aqueous environments are relatively immobile, regardless of oxidation or reduction conditions. Under reducing conditions, other elements, such as V, U, Te, As, Sb, Mo, and Cr exhibit a moderate degree of mobility. The aforementioned elements are likely to be absorbed or adsorbed by clay minerals in the form of metallorganic complexes (White 2003). Tonsteins in the study area are low in P, Ti, Nb, Ta, Hf, V, concentrations, medium to high in REE, Zn, Li, Y, Sr, Zr, Th and U, and have a high Th/U ratio and a distinct negative Eu anomaly. As shown in the scatter diagrams of (Fig. 5), Sabero tonsteins always fall in an isolated distribution area.

Analytical results suggest that the source materials of tonsteins from Sabero tonsteins were probably derived from volcanic eruptions of common magmatic compositions. Based on a comparison of the abundance and assemblage of trace elements between various magmatic rocks, the source materials of tonsteins from Sabero Coalfield were mostly composed of calc-alkaline volcanic ash.

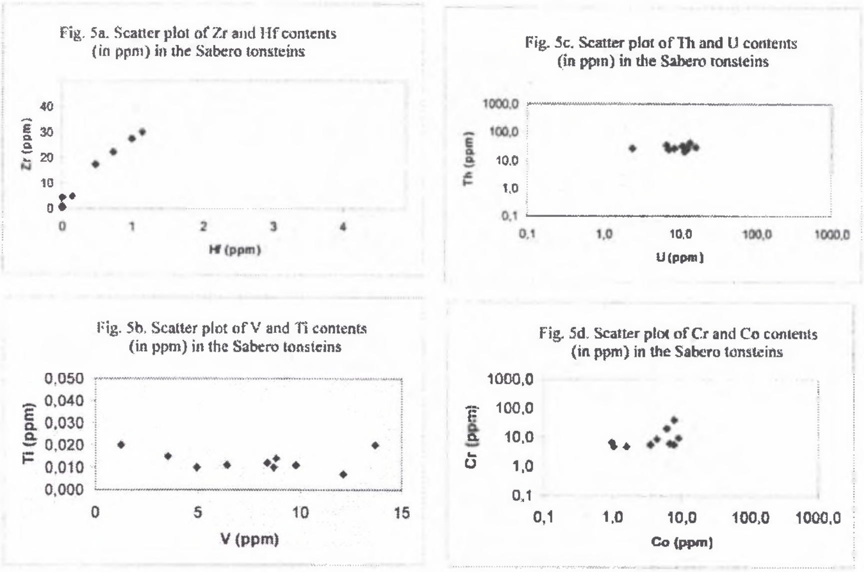
Fig. 5a. Scatter plot of Zr and Hf contents (in ppm) in the Sabero tonsteins

Fig. 5c. Scatter plot of Th and U contents (in ppm) in the Sabero tonsteins

Fig. 5b. Scatter plot of V and Ti contents (in ppm) in the Sabero tonsteins

Fig. 5d. Scatter plot of Cr and Co contents (in ppm) in the Sabero tonsteins

Fig. 5. Scatter plots of chosen analysed elements
Fig. 5. Wykres zawartości wybranych pierwiastków

A comparable volcanic suite occurs in isolated outcrops in the Iberian Cordillera, to the south of the Ebro Valley in NE Spain. This has been described as an essentially calc-alkaline suite ranging between basaltic and rhyolitic end members with common andesite, dacite, and rhyodacite (Munoz et al., 1985). The earliest age for this period of volcanism is as yet imprecise although the sequence is identified as Permo-Carboniferous, in which the earliest sediments are described as post-Westphalian.

The stratigraphy of the Sabero Coalfield have been established on lithostratigraphic and biostratigraphic criteria. However, very tectonised structure of the coalfield has given rise to numerous problems for the identification and correlation of structurally isolated units and groups of coal seams in relation to the recognised stratigraphic succession in the coalfield, and this in turn has reflected the local difficulty of establishing structural relationships. The investigation of the presently of tonsteins has assisted the reinterpretation of a number of structural and stratigraphic problems, which are significant to the Sabero Coalfield (see Knight et al. 2000).

Conclusions

Geochemical data suggest that the tonstein layers within the coal-bearing formation of the Sabero Coalfield are altered, distal, airfall volcanic ashes of common chemistry and origin. Tonsteins in the study area are medium to high concentration in REE, Zn, Li, Y, Sr, Zr, Th and U; wheras, low in concentration Sc, V, Cr, Co, Hf, P,Ta Ni, Nb, Ti and relatively high Th/U ratio as well distinctive Eu anomaly. All this is consistent generally with a silicic magmatic source. Particularly, enrichment of LREE and low content of Hf, Ta, and Ti depletion of indicates rather highly evolved magmas which have incorporated either subcrustal material from the continental plate or subducted sediments high in volatiles. Based on the mentioned data it can be concluded that the Sabero tonsteins were likely derived from a calc-alkaline rhyodacitic to rhyolitic eruptive source.

Acknoledgements

I would like to thank you to dr. J.A. Knight (Derby, UK) for access to the samples from the Sabero Coalfield and introduction to regional geology of Cantabrian Zone. This project was financed by Polish Committee of Scientific Research (KBN) by internal works of the AGH University of Science & Technology no 10.10.140.153.

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