Ti/Zr ratio as a geochemical tool for the correlation of weathered coals from geological formations in two Latin American sedimentary basins

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ABSTRACT

Major and trace element concentrations in fresh and altered coals in outcrops and coalfields from Táchira and Mérida states (Venezuela), as well as from Napo and Pastaza provinces (Ecuador), have been determined to establish inorganic parameters not dependent of weathering effects. Noteworthy is that the Ti/Zr ratio is approximately constant in each sedimentary basin even for great dis-tances (>100 km). Worldwide data of trace elements analysis in coal samples support the stated Ti/Zr ratio constancy in different basins for fresh and weath- ered ones. Therefore, Ti/Zr ratio can be considered a rapid tool to easily identify coal seam correlations.

Key-words: bituminous coal, geochemistry, elemental ratio, correlation, weathering processes

1. Introduction

Coal seam correlation is a basic requirement for mine planning and estimation of coal reserves. The Venezuelan Táchira-Tarra Basin presents several coal seams in two formations of recent age: the Paleocene Los Cuervos Fm, and the late Eoceno–Oligocene Carbonera Fm (Martínez et al., 2001). The distinction between these two formations is difficult following field features, given that they present similar lithologies (both belong to deltaic sedimentary sequences), the outcroppings are usually poor and, finally, tectonics in this area is complicated thereby impeding field correlation. In addition, correlation by means of palinological or paleontological tools is not suitable when accurate and rapid results are required, and, in the same context, weathering processes notably modify proximate analyses; that is, moisture and ash content grows, volatiles and fixed carbon diminish (Martínez and Escobar, 1995).

Similarly, it is also complicated the correlation between coal seams in the Cretaceous sequence of the Ecuatorian Oriente Basin. In this area, the Hollín and Napo formations show also stratigraphically very close coal seams very difficult to correlate (Chiriboga, 2007). Under these circumstances described for the two areas indicated above, geochemical tools based on the analyses of trace elements content and distribution may be very useful. In this regard, numerous elemental ratios have been suggested for coal characterization, namely the Y/La ratio was used to determine preferential directions of clastic inputs in a coalfield (Zubovic, 1966); Na/K, Na/Ca, and Ca/Sr have been used to establish palaeosalinity levels (Krejci-Graf, 1984); Mn/Ti (Ernst, 1970), Ti/Al (Bhatt, 1974), and Na/Al (Slansky, 1985) have been used to estimate the oxygen enrichment in water bodies of precursor peat swamps or mires.

More specifically, with the aim of coal seams correlation within coalfields, a variety of trace elements have been also used (Nicholls and D'Auria, 1979). In addition, statistical methodologies may facilitate the treatment of multi-elemental data to correlate coal

seams, even when they are situated at long distances (O'Connor, 1986). However, these procedures require the recovery of fresh coal samples given that weathering processes mobilize major and trace elements (Miller and Given, 1986). In this sense, in many unexplored zones of the Táchira-Tarra Basin and the Oriente Basin of Ecuador only partially oxidized coals are found within the outcroppings and therefore, the coal seams correlation by trace element ratios is not appropriate as remarked above; that is, weathering modifies the elemental ratios under study (Finkelman, 1993). As a consequence, it is necessary to obtain geochemical parameters of low sensitivity to weathering.

Taking into account the properties of several transition elements such as Ti, Zr, and Hf, and particularly their conservative fate during weathering processes and their immobility in sedimentary, transport, and diagenesis processes (Fralick and Kronberg, 1997), their use as geochemical tool for the correlation of both weathered and fresh coal samples is proposed in this work. As a main hypothesis, it is proposed that Ti and Zr concentrations do not vary significantly as a result of weathering processes.

1. Samples and methods

Twenty-one humic coal samples from the Carbonera Formation in the Táchira and Mérida states (Venezuela) were collected; three additional humic coals from the Hollín Formation were sampled inthe provinces of Napo and Pastaza in eastern Ecuador (Figure 1). The Hollín Fm is composed of sandstones interbedded with siltstones, coaly shales, and coal seams (White et al., 1995); while the Carbonera Fm is mainly composed of shales irregularly interbedded with argillaceous sandstones and coal seams (González de Juana et al., 1980). Eighteen fresh samples were taken from open-cast mines and areas recently exploited by mining works in Jondachi, Zea, Las Mesas, San Simón y Santa Teresa locations; the rest were taken in the Umuquena river and in the surroundings of Puyo (see Figure 1) 60 and they are strongly weathered. The distance between Las Mesas and Santa Teresa is approximately 60 km, whereas Puyo is about 100 km far from Jondanchi.

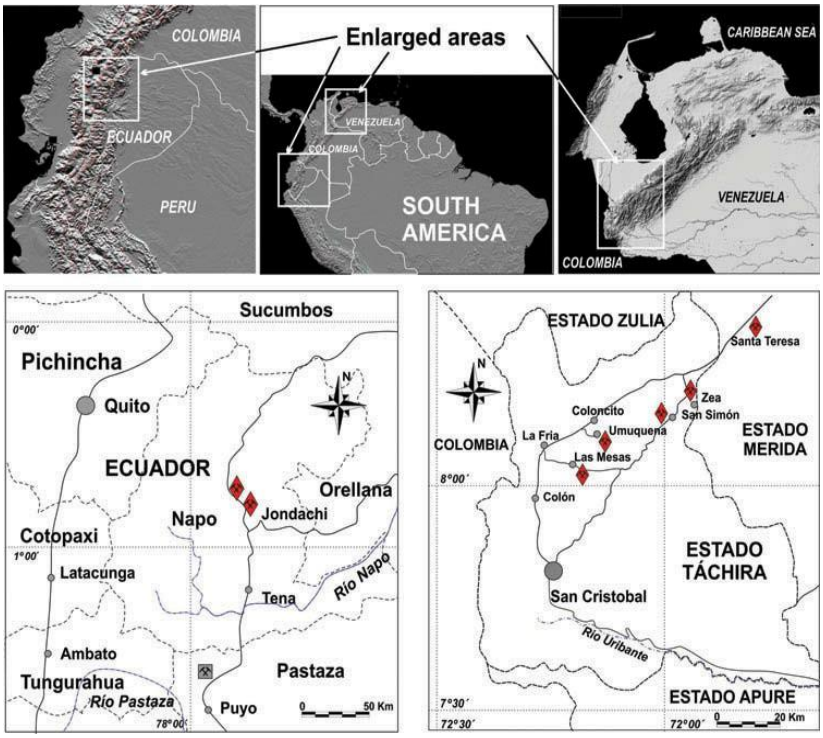

Figure 1. Location of the two study coal basins and sampling sites.

Each sample consisted of approximately 5 kg; initially they were homogenized and then put through a Jones jaw crusher to finally obtain representative 100 g subsamples. The coal samples were analyzed for moisture, volatile matter, and ashes using the standards ISO 687:2010, ISO 562:2010, and ISO 1171:2010,respectively. The fixed carbon was calculated by difference. The degree of alteration/weathering was measured by the flotation method (Marchioni et al., 1981). X-ray fluorescence (XRF) using an energy-dispersive Panalytical Axios equipment was used to determine Ni, Zn, Ti, Zr, and Ca on ashes obtained at 525°C in an open muffle furnace (Hackley et al., 2005). In addition, after the sample digestion process following the method described by Altunsoy et al. (2016), Na and K were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) through a Perkin-Elmer Optima 3000 spectrometer.

The coal samples from Jondachi, Zea, Santa Teresa, San Simón, and Las Mesas locations (samples U1–U2 and F1–F16) are pristine and fresh, without any relevant effect of weathering processes as indicated by the degree of alteration measured (1–14%, Table 1). On the contrary, samples from Umuquena River and Puyo surroundings (A1–A6 and M1) show much more higher degree of alteration (ranging between 29 and 62%), which explains the notably modified data of proximate analyses (Table 1). In this sense, it is noteworthy that altered coals show high values of ash yield (Martínez and Escobar, 1995).

Table 1. Proximate analyses (wt.% on a dry basis), alteration degree of the coal samples and element concentration (mg/kg) in all the coal samples.

	Sampling site	Moisture	Volatile matter	Fixed carbon	Ash yield	Alteration degree	Na	K	Ca	Ti	Zr	Ni	Zn
F1	Zea	9.0	45	44	1.8	6	108	100	300	150	4	30	38
F2	Zea	3.6	58	38	1.5	2	90	600	3,950	200	140	12	6
F3	Zea	10.2	45	44	1.2	2	89	7,400	2,100	4,900	68	–	46
F4	Zea	2.4	40	22	35.4	6	129	15,100	45,050	3,000	56	532	202
F5	Zea	3.0	43	23	31.5	6	135	100	800	2,200	242	6	20
F6	Santa Teresa	9.6	48	39	3.3	8	93	8,400	5,700	8,500	84	378	432
F7	Santa Teresa	1.2	23	45	31.2	4	167	1,700	5,000	2,100	68	–	25
F8	San Simón	8.4	43	32	16.8	12	115	3,200	200	1,300	30	16	24
F9	San Simón	12.6	68	17	2.7	4	134	8,700	10,900	1,350	44	4	–
F10	San Simón	4.2	55	29	12.3	2	156	1,900	38,450	1,250	28	194	6
F11	Las Mesas	1.8	51	46	1.2	2	217	1,100	10,500	1,100	72	6	–
F12	Las Mesas	3.0	64	27	5.7	8	250	100	1,400	5,500	114	932	–
F13	Las Mesas	13.2	62	21	4.2	8	279	1,300	2,900	400	10	4	10
F14	Las Mesas	10.2	69	19	1.8	4	270	1,500	1,600	450	10	–	4
F15	Las Mesas	14.4	62	18	4.8	2	207	1,000	2,950	250	6	–	12
F16	Las Mesas	13.8	64	19	3.3	6	3542	31,800	2,000	200	10	46	–
U1	Jondachi	4.2	40	44	12.3	4	480	2,900	7,300	600	20	26	24
U2	Jondachi	4.8	41	40	14.1	4	444	3,300	6,150	650	21	14	28
A1	Umuquena	2.4	17	6	74.7	62	3696	30,500	2,100	4,000	90	–	–
A2	Umuquena	1.8	27	25	46.2	40	3784	27,400	1,150	2,800	108	–	50
A3	Umuquena	2.4	21	12	64.2	56	104	9,600	850	3,350	100	–	43
A4	Umuquena	3.0	35	31	31.2	28	3544	30,100	2,100	1,250	202	–	72
A5	Umuquena	3.0	20	5	72.6	42	3616	16,950	900	3,650	92	–	24
M1	Puyo	15.6	16	25	42.9	36	6504	31,400	6,950	5,950	190	–	–
Detection limit (LOD)		±0.6	±1	±1	±0.3	±2	±8	±50	±50	±50	±2	±2	±2

Table 2. Elemental ratios in the sampled coals from Ecuador and Venezuela.

	Ti/Zr	Na/K	Na/Ca	Na/Ti	Ca/Ti	Ca/Zn	Na/Zn
F1	33.3	1.083	0.362	1.08	2.0	8	2.8
F2	1.4	0.152	0.023	0.45	19.9	650	15.0
F3	71.0	0.012	0.042	0.02	0.4	46	1.9
F4	52.6	0.008	0.003	0.04	15.1	223	0.6
F5	9.1	1.351	0.171	0.06	0.3	38	6.4
F6	100.0	0.012	0.022	0.01	0.7	13	0.2
F7	30.9	0.101	0.033	0.08	2.4	200	6.7
F8	43.3	0.040	0.580	0.09	0.2	9	5.0
F9	30.2	0.023	0.015	0.10	8.1	–	–
F10	44.6	0.081	0.004	0.12	31.0	7680	31.2
F11	15.3	0.202	0.021	0.20	9.9	–	–
F12	47.8	2.501	0.182	0.05	0.3	–	–
F13	36.4	0.214	0.103	0.70	7.2	290	27.9
F14	44.4	0.180	0.171	0.68	4.0	400	67.5
F15	40.0	0.211	0.072	1.04	14.9	223	15.9
F16	18.2	0.113	1.770	17.71	10.0	–	–
U1	30.0	0.165	0.066	0.80	12.2	304	20.0
U2	30.9	0.123	0.072	0.68	9.5	219	15.9
A1	44.4	0.122	1.760	0.92	0.5	–	–
A2	25.9	0.143	3.443	1.35	0.4	22	75.6
A3	33.5	0.011	0.142	0.04	0.3	19	2.5
A4	6.2	0.121	1.691	2.96	1.7	29	49.3
A5	39.6	0.210	4.013	1.00	0.3	38	150.5
M1	31.3	0.207	0.941	1.09	1.2	–	–

Table 1 also shows significant variations in elemental concentrations. The altered coals exhibited a notable depletion of Ni and a low to moderate enrichment of Na, K, Ca, Ti, Zr, and Zn. Also, some elemental ratios were calculated (Table 2).

Additionally, Table 3 shows the median (Mdn) value, interquartile range (IQR) and IQR/Mdn quotient for each of the elemental ratios from the two groups (fresh and altered) of Venezuelan samples, as well as the mean (μ) value, standard deviation (σ), and coefficient of variation (CV) for

each of the elemental ratios from the fresh Ecuadorian coal samples. In the case of Venezuelan samples, the median was used because it is a robust measure of central tendency (better than the mean). In fact, it shows low sensitivity to both high and low anomalous values that can dramatically affect the mean. Also, the IQR/Mdn quotient was used to measure the extent of variability in relation

to the median value of the populations. The Ti/Zr values are relatively similar both in fresh and weathered samples, and therefore it does not seem to be affected by weathering processes.

2. Discussion

It is well-known that Ti and Zr have a strong inorganic affinity (Bouska, 1981). For instance, Ti/Zr values in the earth crust are around 30; for shales, the ratio is close to 25, whereas in other rocks such as granite it varies between 12 and 64 (Krauskopf, 1979), thereby showing that it is influenced by the

Table 3. Statistical data from elemental ratios in fresh and weathered sampled coals.

	Venezuelan fresh samples			Venezuelan altered samples			Ecuadorian fresh samples		
Ratio	Mdn	IQR	IQR/Mdn	Mdn	IQR	IQR/Mdn	μ	σ	CV
Ti/Zr	38.2	22.0	0.57	39.6	13.7	0.41	30.45	0.45	0.01
Na/K	0.13	0.16	1.23	0.122	0.022	0.18	0.14	0.02	0.14
Na/Ca	0.06	0.15	2.58	1.76	1.75	0.99	0.069	0.003	0.05
Na/Ti	0.11	0.63	5.77	1.00	0.43	0.43	0.74	0.06	0.08
Ca/Ti	5.63	11.90	2.11	0.40	0.20	0.50	10.85	1.35	0.13
Ca/Zn	211.5	319.5	1.51	25.5	13.0	0.51	261.5	42.5	0.16
Na/Zn	6.60	17.2	2.61	62.4	87.2	1.40	17.95	2.05	0.12

Table 4. Average values of Ti/Zr, Ti, and Zr (mg/kg) in coal samples from the world, China, and the entire United States, as well as several regions and states in the United States, as well as the same data, ash yield (%db) and total sulfur (St, %daf) in five sample sets from the Herrin coal seam No. 6 in the Illinois Basin.

	Ti	Zr	Ti/Zr	St	Ash yield	Reference
World averages for 26 ash yields of bituminous coals	3,200	115	28	–	–	Yudovich et al. (1972)
Geometric means in US coals (over 7,000 samples)	600	19	32	–	–	Finkelman (1993)
Geometric means in 28 coals from western USA	500	26	19	–	–	Gluskoter et al. (1977)
Geometric means in 23 coals from the Appalaches	900	41	22	–	–	Gluskoter et al. (1977)
Geometric means in 114 coals from the Illinois Basin	600	41	15	–	–	Gluskoter et al. (1977)
Average values for 4 US fresh coals from Wyoming	575	21	27	–	–	Gluskoter et al. (1977)
Average values for 2 US weathered coals from Wyoming	600	22	27	–	–	Gluskoter et al. (1977)
Average values for 5 US fresh coals from North Dakota	260	22	12	–	–	Gluskoter et al. (1977)
Average values for 3 US altered coals from North Dakota	300	25	12	–	–	Gluskoter et al. (1977)
World average values in 112 hard coals	890	36	25	–	–	Ketris & Yudovich (2009)
World average values in 74 brown coals	720	35	21	–	–	Ketris & Yudovich (2009)
Average values for 1,322 Chinese coals	1,976	90	21	–	–	Dai et al. (2012)
Average values for 8 channel samples from site 1 (SE Illinois)	550	33.5	16	5.45	13.05	Gluskoter et al. (1977)
Average values for 7 channel samples from site 2 (SE Illinois)	610	36.4	17	4.61	13.01	Gluskoter et al. (1977)
Average values for 6 channel samples from site 3 (SW Illinois)	520	18.1	29	0.76	7.48	Gluskoter et al. (1977)
Average values for 7 channel samples from site 4 (SW Illinois)	570	34.1	17	3.54	13.9	Gluskoter et al. (1977)
Average values for 7 channel samples from site 5 (NW Illinois)	600	29.2	21	3.09	8.9	Gluskoter et al. (1977)

lithological composition of the sediment-source region. As shown in Table 4, all the Venezuelan samples revealed Ti/Zr values of about 40, the strongly weathered sample from Ecuador 31.3 and the Ecuadorian fresh samples showed a Ti/Zr value of ~30 on average. Neither other elemental ratio nor geochemical parameter of those studied in fresh and weathered coals displayed a lower extent of variability in relation to the central value of the populations (Martínez and Escobar, 1995).

The negligible mobility of Zr and Ti can be the reason for the highly similar values of Ti/Zr measured in this work. Even though both elements could be slightly enriched after oxidation of organic matter in coaly sediments, the Zr/Ti ratio would not vary significantly. Thus, oxidative- hydrolytic breakdown of coal does not modify these two transition elements' concentrations, whose predominant source minerals in coal are rutile or anatase and zircon, respectively (Valkovic, 1983). In fact, these mineral phases remain unaltered as immobile components within the inorganic coal fraction even when weathering processes are intense. Consequently, the Ti/Zr ratio can be proposed as a geochemical tool to establish lateral correlation of coal seams and sedimentary rock sequences, specifically when coals have suffered weathering. This conclusion is supported by many other previous works; for example, Table 4 shows several geometric mean values of Ti and Zr in bituminous coals from worldwide (Yudovich et al., 1972) and the entire United States (Gluskoter et al., 1977; Finkelman, 1993), including coals from the Western, Appalachian, and Illinois coal basins. In addition, Ketris and Yudovich (2009) reported world average contents for both elements in brown coals and hard coals (see also Table 4). Recently, Dai et al. (2012) analyzed Ti and Zr contents in Chinese coals. Although in some of these cases it was not directly mentioned if the coal samples were fresh or weathered, this was clearly evident taking into account the high levels of moisture and ash contents for part of the samples. All things together, the Ti/Zr values range from 13 to 32 for the different sets of coal samples studied, as shown in Table 4. If it is considered that both elements show an inorganic association in coals (Valkovic, 1983), these aforementioned data corroborate that Ti/Zr can be used as a geochemical tool in correlation of coal samples whenever those belong to a common sedimentary basin. However, this is only accurate if the sediment-source region was invariably of sedimentary, felsic, or mafic composition.

As also shown in Table 4, another additional support can be obtained from the analyses of a series of samples from the Herrin coal seam No. 6 in five locations within the US Illinois Basin (Gluskoter et al., 1977). This set of coal samples was selected because it had many different features, and samples were not homogeneous; that is, notable dispersion of total sulfur content, opencast and underground

mining, non-marine and marine-influenced underlying-rocks. In addition, the five sampling sites were up to a maximum distance of 305 km. Table 4 shows Ti and Zr contents, ash yield, and total sulfur, together with mean values of Ti/Zr measured in the five locations mentioned; four of them revealed very similar Ti/Zr ratios (16, 17, 17, and 21), while only at the site with a remarkable lower total sulfur content the Ti/Zr is significantly different (29). This can be attributed to a notable paleo- environmental change within the Illinois Basin (less marine influence) and the subsequent variation in lithological composition of the inorganic input from the sediment-source region.

3. Conclusions

The results of this study on the sampled coal occurrences in western Venezuela and eastern Ecuador lead to the following conclusions:

- Contents of several trace elements in coal and combination of elemental ratios have been considered in order to correlate coal seams. Only the ratio Ti/Zr is stable both for fresh and weathered coals.
- The stability of Ti/Zr in weathered samples can be considered of low analytical cost and rapid geochemical tool for correlation of coal seams during both prospecting and exploitation activities.

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