APPENDIX A

Calculations of F^- Content in Coal Samples

Ion chromatographic Technique

According to the procedure in Section 2.4.6.2-1(a), the original samples #20 referring to 0.9996 g of sample was extracted with DMSO/KNO_3 and adjusted with deionized water to the mark of a 50 ml volumetric flask. Then 1.0 ml was pipetted into 100 ml volumetric flask and diluted with deionized water to sample #20 solution.

Weight of samples #20 in sample solution $= 0.9996 \times 10^{-2}$ g/50 ml

From calibration curve:

Concentration of F^- in sample solution $= 0.596$ ng/μl

So, 50 ml of sample solution contained F^- $= 0.596 \times 50$ μg

$= 2.98 \times 10^{-5}$ g

sample #20 0.9996×10^{-2} g contained F^- $= 2.98 \times 10^{-5}$ g

sample #20 100 g contained F^- $= \dfrac{2.98 \times 10^{-5} \times 100}{0.9996 \times 10^{-2}}$ g

$= 0.30$ g

$\therefore$ F^- content in sample #20 $= 0.30$ %w/w

Calculations of Fe^{3+} Content in geological reference materials

Ion chromatographic Technique

Soil 5

According to the procedure in Section 2.5.7.2-Methode II, the original samples #22 referring to 0.0994 g of sample was dissolved with 50 % HNO_3 and adjusted with deionized water to the mark of a 25 ml volumetric flask. Then the sample solution was diluted 20-fold with deionized water.

Weight of samples #22 in sample solution was diluted 20-fold	= 0.0994/20	g
	= 4.97×10^{-3} g/25	ml
From calibration curve:		
Concentration of Fe^{3+} in sample solution	= 2.46	ng/µl
So, 50 ml of sample solution contained Fe^{3+}	= 2.46 x 25	µg
	= 6.15×10^{-5}	g
sample #22 4.97×10^{-3} g contained Fe^{3+}	= 6.15×10^{-5}	g
sample #22 100 g contained Fe^{3+}	= $\frac{6.15 \times 10^{-5} \times 100}{4.97 \times 10^{-3}}$	g
	= 1.24	g
$\therefore$ Fe^{3+} content in sample #22	= 1.24	%w/w

APPENDIX B

Radii in Angstrom units (A) of selected atoms and ions.

F	0.64	Cl	0.99	Br	1.14
F^-	1.36	Cl^-	1.81	Br^-	1.95

Mn	1.29	Fe	1.26	Cu	1.28	Pb	1.75
Mn^{2+}	0.80	Fe^{2+}	0.76	Cu^+	0.96	Pb^{4+}	0.84
Mn^{3+}	0.66	Fe^{3+}	0.64	Cu^{2+}	0.72	Pb^{2+}	1.32
Co	1.25	Ni	1.24	Zn	1.33		
Co^{2+}	0.74	Ni^{2+}	0.69	Zn^{2+}	0.74		

Source : Wall Chart entitled "Relative Sizes of Atoms and Ions in the Periodic Table", Sargent-Welch Scientific Co., 1970.

NO_2^-	1.55	SO_4^{2-}	2.30
NO_3^-	1.89	PO_4^{3-}	2.38

Source : Shriver, D.F., Atkins, P.W. and Longford, C.H., Inorganic Chemistry, Oxford University Press, Oxford, 1994, p.173.

APPENDIX C

Properties of Some Metal-PAR Species.

Table C-1 Properties of Some Metal-PAR Species[a]

	Approx. pH	M:PAR	λ_{max} (nm)	$\in$ x 10^{-3}
Au(III)		1:1	540	8.3 (tert-butanol + xylene)
Bi	1	1:1	515	10.7
Cd	10	1:2	495	57.8
Co(III?)		1:2	510	5.5
Cu(II)[b]	2 ; 7 ; 10	1:1 (pH 2.3-5)	522	12.1
		1:2 (pH>5)	505-510	58.9
Ga	4 ; 7	1:1 (pH 1.5-3)	490-495	21.2
		1:2 (pH 3-5)	500-505	9.9
Hf		1:4 (pH2.5)	510	37.5 (isoamyl alcohol)
In	7	1:1	500-510	32.8
Mn	10	1:2	496	86.5
Nb	5-6	1:1 (0.1-0.2 *N* H_2SO_4)	530	18
		1:1 (pH~6)	555	38.7 , 31.2
Pb	10	1:1	512	10.8
		1:2	522	50.2
Pd	6 ; H_2SO_4 soln.	1:1 (H_2SO_4 solution)	440	18.4
Pt(II)	3	1:1	450, 660	22.9
Rare earths	6-7	1:2	515	~16 to 50
Sc	3-5	1:1(pH 2)	505 (515)	14.7 (22.1)
Ta	5	1:1	515	20.4
Th	7	1:4	500	38.9

Table C-1 Properties of Some Metal-PAR Species[a] (Cont.)

	Approx. pH	M:PAR	λ_{max} (nm)	$\in$ x 10^{-3}
Tl(III)[c]		1:1	520	18-19.4
U(VI)	7-8	1:1	510 (530)	38.5
V(V)	6.5	1:1	~550	
Zn	8		495	81
Zr		1:1 (pH 4)	535	21

Source : [a] Condensed from Busev and Ivanov, *loc. city.*, with later data from other authers. Solvent: H_2O.

[b] O.A. Tataev, S.A. Akhmedov, and Kh.A. Akhmedova, *Zh. Anal. Khim.*, 24, 834(1969), report formation of a 1:1 complex at pH 1.5-2.5, $\in_{540} = 27{,}000$.

[c] As shown by E.A. Biryuk and R.V. Ravitskaya, *Zh. Anal. Khim.*, 26, 1767 (1971), Tl(III) forms $Tl(OH)_2L$ (HL = PAR and PAN).

APPENDIX D

Table D-1 Values of t for ν Degree of Freedom for Various Confidence Levels

ν	Confidence Level, %	90	95	99	99.5
1		6.314	12.706	63.657	127.32
2		2.920	4.303	9.925	14.089
3		2.353	3.182	5.841	7.453
4		2.132	2.776	4.604	5.598
5		2.015	2.571	4.032	4.773
6		1.943	2.447	3.707	4.317
7		1.895	2.365	3.500	4.029
8		1.860	2.306	3.355	3.832
9		1.833	2.262	3.250	3.690
10		1.812	12.228	3.169	3.581
15		1.753	2.131	2.947	3.252
20		1.725	2.086	2.845	3.153
25		1.708	2.060	2.787	3.078
α		1.645	1.960	2.576	2.807

Source : Christian, G.D., Analytical Chemistry, 3rd ed., John Wiley & Sons, New York, 1980, p.71.

APPENDIX E

Detail about geological reference materials

Detail about geological reference materials in this work

Symbol

- = precision of compiled data established to be better than 10% relative (two sigma) normally based on five or more results from two or more independent techniques.

? = additional uncertainly, caused, for example, by a large disparity in reported results, and/or a small number of reported results (usually < 3) and/or data derived from only one "non-definitive" analytical technique.

calc = Value calculated from quoted data, normally assuming oxide stoichiometry

cv = Datum quoted as a certified value by the distributing organization.

Soils

wt.%	GSS tropical soil CS-1	GSS tropical soil K-3	GSS tropical soil SAu-1	GSS tropical soil SUR-1	IAEA soil SOIL-5	IAEA soil SOIL-7
SiO_2	45.00	47.75	42.40	45.30	71 ?	38.5 ?
TiO_2	1.06	1.83	1.80	0.93	0.78 ?	0.5 ?
Al_2O_3	17.00	23.00	20.50	14.90	**15.48**	8.9 ?
Fe_2O_3	-	-	-	-	-	-
FeO	-	-	-	-	-	-
MnO	0.05	0.04	0.10	0.04	**0.110**	0.0815 cv
MgO	0.19	0.05	0.11	0.10	2.5 ?	1.37 ?
CaO	0.05	0.02	0.04	0.03	3.1 ?	22.8 ?
Na_2O	0.10	0.10	0.04	0.01	**2.59**	0.32 ?
K_2O	0.50	0.03	0.05	0.11	**2.24**	1.46 ?
P_2O_5	0.07	0.05	0.08	0.06	0.25 ?	0.105 ?
H_2O^+	-	-	-	-	-	-
H_2O^-	-	-	-	-	-	0 dried
CO_2	-	-	-	-	-	-
C	-	-	-	-	-	-
SUM Tr.	0.19	0.20	0.27	0.23	0.33	0.16
Total	64.21	73.07	65.39	61.71	98.38	74.69
Fe_2O_3T	24.70	14.73	21.90	28.40	**6.36**	3.67 ?
L.O.I.	11.25	11.60	12.20	10.10	0 calc	0 calc
XTotal	99.97	99.20	99.22	99.98	104.41	78.21
REF	BUR85	BUR85	BUR85	BUR85	DYB79	IAEA84

ppm	CS-1	K-3	SAu-1	SUR-1	SOIL-5	SOIL-7
Ag	-	-	-	-	1.9 ?	-
As	8	2.3	4	11	94	13.4 cv
Au	0.33 ?	-	0.2 ?	0.3 ?	-	-
B	-	-	-	-	63 ?	-
Ba	220	27	50	45	**562**	159 ?
Be	-	0.2 ?	0.6 ?	0.3 ?	1.8 ?	-
Bi	0.6 ?	34 ?	8 ?	11 ?	12 ?	-
Br	5.9 ?	3.8 ?	6.6 ?	4.3 ?	5.4	7 ?
Cd	15 ?	-	16 ?	15 ?	1.5 ?	1.3 ?
Ce	*27.7* pot91	*56.4* pot91	*18.8* pot91	*13.5* pot91	**59.7**	61 cv
Cl	50 ?	12 ?	250 ?	-	-	-
Co	-	-	35	24	**14.8**	8.9 cv
Cr	500	200	640	500	**28.9**	60 cv
Cs	*1.27* pot91	0.32 ?	*0.6* pot91	*0.9* pot91	**56.7**	5.4 cv
Cu	110	45	150	74	**77.1**	11 cv
Dy	-	-	-	-	4.0	3.9 cv
Er	-	-	-	-	-	-
Eu	*0.63* pot91	*0.56* pot91	*0.50* pot91	*0.37* pot91	**1.18**	1.0 cv
F	-	180 ?	-	50 ?	628 ?	480 ?
Ga	-	19 ?	-	-	**18.4**	10 ?
Gd	-	-	-	-	35 ?	-
Ge	-	-	-	-	2.3 ?	-

Soils

ppm	CS-1	K-3	SAu-1	SUR-1	SOIL-5	SOIL-7
Hf	*4.55* pot91	*15.5* pot91	*3.8* pot91	*3.58* pot91	6.30	5.1 cv
Hg	-	-	-	-	0.79 ?	0.04 ?
Ho	-	-	-	-	0.82 ?	1.1 cv
I	-	-	-	-	35 ?	-
In	-	2 ?	-	-	-	-
Ir	-	-	-	0.007 ?	-	-
La	12	16	6 ?	6 ?	28.1	28 cv
Li	18 ?	12 ?	2 ?	13 ?	52.1 ?	31 ?
Lu	*0.23* pot91	*0.26* pot91	*5.6* pot91	*6.0* pot91	0.336	0.3 ?
Mo	24	5	18 ?	-	1.7 ?	2.5 ?
N	-	-	-	-	-	-
Nb	-	-	-	-	9 ?	12 ?
Nd	*11.4* pot91	*13.4* pot91	*6.5* pot91	-	29.9	30 cv
Ni	62	43	80	60	13 ?	26 ?
Os	-	-	-	-	-	-
Pb	17	17	12 ?	10 ?	129	60 cv
Pd	-	-	-	-	-	-
Pr	-	-	-	-	5.0 ?	-
Pt	-	-	-	0.15 ?	-	-
Ra Bq/g	-	-	-	-	-	-
Rb	7.3 ?	5.7 ?	9 ?	8 ?	138	51 cv
Re	-	-	-	-	-	-
Rh	-	-	-	0.02 ?	-	-
Ru	-	-	-	-	-	-
S	-	500 ?	600 ?	600 ?	-	-
Sb	1 ?	-	0.9 ?	1 ?	14.3	1.7 cv
Sc	*40.7* pot91	*30.1* pot91	*62.0* pot91	*39.9* pot91	14.8	8.3 cv
Se	2.2 ?	1.5 ?	-	1.6 ?	1.3 ?	0.4 ?
Sm	*2.18* pot91	*2.58* pot91	*1.58* pot91	*1.31* pot91	5.42	5.1 cv
Sn	-	1.3 ?	-	5 ?	4.2 ?	-
Sr	23	10	9	7	330 ?	108 cv
Ta	*0.64* pot91	*1.14* pot91	*0.53* pot91	*0.49* pot91	0.764	0.8 cv
Tb	*0.38* pot91	*0.34* pot91	*0.43* pot91	*0.31* pot91	0.665	0.5 cv
Te	-	-	-	-	-	-
Th	*8.3* pot91	*9.9* pot91	*3.3* pot91	*6.9* pot91	11.3	8.2 cv
Tl	-	-	-	-	-	-
Tm	-	-	-	-	0.42 ?	-
U	*0.9* pot91	*1.5* pot91	*1.26* pot91	*1.9* pot91	3.15	2.6 cv
V	450	220	460	600	151 ?	66 cv
W	10	-	-	2 ?	5.1 ?	-
Y	9 ?	5 ?	8 ?	6 ?	21 ?	21 cv
Yb	*1.35* pot91	*1.62* pot91	*1.32* pot91	*1.04* pot91	2.24	2.4 cv
Zn	65	50	105	60	368	104 cv
Zr	150	500	115	110	221 ?	185 cv
REF	BUR85	BUR85	BUR85	BUR85	DYB79	IAEA84

Sediments

wt.%	BAS ball clay BCS 348	BCR estuarine sediment CRM 277	BCR lake sediment CRM 280	BCR river sediment CRM 320	BSRRM grey shale AWI-1	BSRRM micaceous siltite PRI-1
SiO_2	**51.1** cv	-	-	-	**60.35**	**68.63**
TiO_2	**1.08** cv	-	-	-	**0.91**	**0.72**
Al_2O_3	**31.6** cv	-	-	-	**16.55**	**10.89**
Fe_2O_3	**1.04** cv	-	-	-	1.30	1.01
FeO	-	-	-	-	5.26	2.04
MnO	-	0.19 cv	0.17 cv	0.10 cv	0.14	0.04
MgO	**0.30** cv	-	-	-	2.00	3.12
CaO	0.17 cv	-	-	-	0.67	2.44
Na_2O	0.34 cv	-	-	-	**0.76**	1.73
K_2O	**2.23** cv	-	-	-	**3.07**	3.77
P_2O_5	0.071 cv	-	-	-	0.15	**0.19**
H_2O^+	-	-	-	-	-	-
H_2O^-	0 dried	-	-	-	0 dried	0 dried
CO_2	-	-	-	-	1.46 ?	2.62 ?
C	1.64 T	-	-	-	-	-
SUM Tr.	0.07	0.17	0.16	0.14	0.33	0.22
Total	89.66	-	-	-	92.95	97.42
Fe_2O_3T	**1.04** cv	-	-	-	**7.14**	**3.28**
L.O.I.	**11.8** cv	-	-	-	**7.70**	**4.99**
XTotal	99.75	-	-	-	99.44	99.80
REF	BAS89	BCR	BCR	BCR	ROE88	ROE88

ppm	BCS 348	CRM 277	CRM 280	CRM 320	AWI-1	PRI-1
Ag	-	-	-	-	-	-
As	-	47.3 cv	51.0 cv	76.7 cv	15.9	13 ?
Au	-	-	-	-	-	-
B	-	-	-	-	161	54 ?
Ba	360 ?	329 ?	617 ?	531 cv	384	510
Be	-	-	-	-	-	-
Bi	-	-	-	-	-	-
Br	-	87 ?	11 ?	-	-	-
Cd	-	11.9 cv	1.6 cv	0.53 cv	-	-
Ce	-	-	70 ?	95 ?	**82.4**	79
Cl	-	-	-	-	-	-
Co	-	17 ?	20 ?	19 ?	21.2	6.5
Cr	110	192 cv	114 cv	138 cv	**117**	76
Cs	-	-	-	-	6.8 ?	2.2 ?
Cu	-	101.7 cv	70.5 cv	44.1 cv	36	3 ?
Dy	-	-	-	-	4.2	3.5
Er	-	-	-	-	-	-
Eu	-	-	-	-	**1.53**	**1.28**
F	-	-	-	-	577 ?	394 ?
Ga	-	-	-	-	24 ?	18 ?
Gd	-	-	-	-	5.6	4.9
Ge	-	-	-	-	-	-

Sediments

ppm	BCS 348	CRM 277	CRM 280	CRM 320	AWI-1	PRI-1
Hf	-	-	-	-	6.12	10.7
Hg	-	1.77 cv	0.670 cv	1.03 cv	-	-
Ho	-	-	-	-	0.9 ?	1.0 ?
I	-	-	-	-	-	-
In	-	-	-	-	-	-
Ir	-	-	-	-	-	-
La	-	45 ?	39 ?	46 ?	**38.2**	**37.3**
Li	-	-	-	-	-	-
Lu	-	-	-	-	0.46	0.39
Mo	-	-	-	-	-	-
N	-	-	-	-	-	-
Nb	-	-	-	-	-	-
Nd	-	-	-	-	37.5	37.6
Ni	-	43.4 cv	73.6 cv	75.2 cv	66	22
Os	-	-	-	-	-	-
Pb	-	146 cv	80.2 cv	42.3 cv	22	12
Pd	-	-	-	-	-	-
Pr	-	-	-	-	-	-
Pt	-	-	-	-	-	-
Ra Bq/g	-	-	-	-	-	-
Rb	-	-	-	-	130	**88**
Re	-	-	-	-	-	-
Rh	-	-	-	-	-	-
Ru	-	-	-	-	-	-
S	-	-	-	-	869	170 ?
Sb	-	4.0 ?	1.4 ?	0.6 ?	0.74 ?	0.24 ?
Sc	-	9.0 cv	12.8 cv	15.25 cv	16.3	9.49
Se	-	2.04 cv	0.68 cv	0.214 cv	-	-
Sm	-	-	-	-	**7.1**	**6.6**
Sn	-	-	-	-	7 ?	2 ?
Sr	-	-	-	-	107	87
Ta	-	-	-	-	1.37	1.06
Tb	-	-	-	-	0.91	0.77
Te	-	-	-	-	-	-
Th	-	9.0 ?	15 ?	18 ?	12.2	12.1
Tl	-	-	0.7 ?	0.5 ?	-	-
Tm	-	-	-	-	0.18 ?	0.29 ?
U	-	-	-	-	3.1	2.49
V	-	102 ?	101 ?	105 ?	141	72
W	-	-	-	-	-	-
Y	-	-	-	-	32 ?	21 ?
Yb	-	-	-	-	3.00	2.40
Zn	-	547 cv	291 cv	142 cv	100	41
Zr	220 ?	-	-	-	223	382
REF	BAS89	BCR	BCR	BCR	ROE88	ROE88

Reference to source data.

fug 85 = R. Fuge (1985)

ter 84 = S. Terishima (1986)

vic 86 = A.H. Victor (1986)

Cro 82 = I. Croudace, J.-L. Joron, H. Jaffrezic, G. Meyer and Treuil (1982)

ran 89 = K.R. andle and I.W. Croudace (1989)

roe 85 = I. Roelandts, G. Robaye, G. Weber and J.M. Delbrouck (1985)

els 87 = H.N. Elsheimer (1987)

vic 80 = A.H. Victor and F.E.W. Strelow (1980)

Source : P.J. Potts, A.G. Tindle and P.C. Webb, *Geochemical Reference Material Composition*, Whittles, London, 1992, pp.(54-55) and (84-85).

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