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CRB Analyse Service GmbH

IWG - ZW-C, Zinnwaldit

Veranstalter: International Workinggroup Geostandards (IWG) of the Association Nationale de la Recherche Technique, Paris

Ringversuchsmaterial: Zinnwaldit ZW-C (Lithiumglimmer)

RV geschlossen: 1993 – 6

Literatur: GEOSTANDARDS NEWSLETTERS, Vol. 18, No. 1, 1994

Hauptelemente [MA%]

	CRB	RV	1sRV	Z-Score
Na_2O	0,27	0,33		
MgO	0,17	0,16		
Al_2O_3	18,33	18,45		
SiO_2	52,97	54.00		
P_2O5	0,02	0,025		
SO_3	0,046	0,045		
K_2O	7,75	7,72		
CaO	0,36	0,37		
TiO_2	0,043	0,05		
Fe_2O_3 tot	9,28	9,46		
MnO	0,746	0,75		

Spurenelemente [µg/g]

	CRB	RV	1sRV	Z-Score
Ba	112	52		
Cd	1,3	1,5		
Ce	74	97		
Cl	43	30		
Co	8	2		
Cr	47	56		
Cu	44	39		
F	65900	54500		
Ga	104	99		
La	32	30		
Ni	12	11		
Pb	107	80		
Rb	8458	8500		
Sr	18	17		
U	24	20		
V	4	6		
W	321	320		
Y	61	33		
Zn	1029	1050		

Zr	39	82

Legende

CRB: Ergebnisse CRB – **RV:** Ergebnisse Ringversuch -- **1s-RV:** Standardabweichung Ringversuch
Z-Score: Differenz des Messwertes vom Mittelwert des Ringversuchs -- * Wert nicht zertifiziert

1994 Report on Zinnwaldite ZW-C Analysed by Ninety-Two GIT-IWG Member-Laboratories

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Within a short period of one year (November 1992-October 1993), ninety-two IWG-Member laboratories have been able to characterize the chemical composition of a candidate reference sample, Zinnwaldite ZW-C, a Li-mica, reputed difficult to analyse because of its high contents of F and rare alkali elements and of the presence of refractory minerals. Thanks to the help of 163 analysts from the 92 laboratories, it has been possible to assign working values for 20 major and minor elements including the rare alkali elements and for 43 trace elements; all the working values receive the status of recommended values, except H_2O, CO_2, LOI, Cl and S. It is, indeed, a rare success for such a difficult sample!

The collaborative study of Zinnwaldite ZW-C was launched in November 1992 and it lasted for one year. For us, it is really an immense pleasure to state that ninety-two IWG Member-Laboratories have participated, with success, in the chemical characterization of ZW-C, a sample, which from the start was considered to be a "difficult" sample to analyse because of its high contents of F and rare alkali elements and also to be a troublesome one to dissolve because of the presence of refractory minerals such as cassiterite, wolframite and topaz. Despite these unfavorable first impressions, 163 analysts have contributed 1090 results on major and minor elements including Li_2O and F and 1700 results on trace elements. Before proceeding further, we wish to extend here our grateful thanks to all these disinterested analysts and to their Laboratory Managers. It is also gratifying to note that most of these analysts continue to participate willingly and regularly in almost all IWG geostandards projects.

The following pages are arranged in four principal sections:

- Sample processing
- Presentation of compiled data
- Evaluation of compiled data
- Final remarks.

All symbols and abbreviations used in the main text, Tables and Appendices are grouped in Table 1. In addition, Table 1 presents an index to the page numbers of Tables and Appendices.

SAMPLE PROCESSING

Most of the IWG reference samples have been entirely processed by the CRPG. With time, the processing of candidate reference samples is also becoming an international co-operation. The Zinnwaldite ZW-C is the first example of a series of samples to follow which have been prepared in other countries. The preparation of a zinnwaldite, a Li-mica, was proposed by Ivan Rubeška of the Czech Geological Survey in July 1989 as a companion sample to the two micas prepared by the CRPG in 1967-1968: Biotite Mica-Fe and Phlogopite Mica-Mg (1).

Description

The Zinnwaldite has been prepared by the Czech Geological Survey from the classical tin-tungsten deposit of Cinovec (Zinnwald) in the Czech Republic. The ore deposit is situated in northern Bohemia about 11 km NNE of the presented in blocks, each block separating one element from the following one.

Each line of data contains four segments. The first segment contains the element/sample information; the second segment presents the concentration of the element (% or ppm) and the third segment shows how it was determined with a three-letter code, explained in Table 1. The last segment points to the laboratory number in three digits, listed in Appendix I; the lower case letter attached to the laboratory number gives additional information on the analyst(s) or modifications of the analytical method.

Wherever possible, each block of data begins with a line heading loaded with the name of element, its working value and the number of data compiled for that element. The line heading in **boldface** presents the recommended value and in normal style the proposed value.

EVALUATION OF COMPILED DATA

Our way of evaluating compiled data has evolved with time and experience and it has been explained in previous reports (ex. 2); it is essentially statistic to start with but tends to become subjective in the end with analytical knowledge overruling statistical figures. A fuller discussion of this topic, with case studies by several "geostandardists", can be found in a recent book (3).

For statistical evaluation, a spreadsheet software (Excel) was used. Excel macro programs have been developed for calculating and tabulating automatically, from "raw" data, statistical parameters such as $\overline{X}a$, s, sk, M, MG, $\overline{X}p$, $\overline{X}geo$ and $\overline{X}cm$. Such calculations are made not only on the total set of data (TT) but also on the sub-sets of data obtained by different groups of analytical methods. Mainly, robust central values such as M, MG, $\overline{X}p$, $\overline{X}geo$ and $\overline{X}cm$, calculated for TT and for individual groups of methods (AA, CC, FX, MN, SF, SG, SM, SP) shed some light on the vicinity of the true value. $\overline{X}pcv$ was calculated when the number of data permitted it and the $\overline{X}pcv$ was often assigned as the working value. In some cases, the $\overline{X}pcv$ of only two or three chosen methods was assigned as the working value and, at times, only one CV (usually, M or $\overline{X}cm$) or even one simple value can come to be chosen as the best value.

Tables 7 to 8 contain the statistical parameters calculated respectively for major and minor elements and for trace elements. Readers interested in their own personal evaluation of compiled data can use these parameters; they can, of course, process also the whole set of data with their proper statistical tools or seek help from the case studies mentioned earlier (3).

Table 9. Zinnwaldite ZW-C. Working values, recommended values in **bold face** and proposed values in *italics*

Major and minor elements			Trace elements		
%	WV	N	ppm	WV	N
SiO_2	**54.00**	81	As	**31**	28
Al_2O_3	**18.45**	88	Ba	**52**	56
Fe_2O_3	**1.30**	28	Be	**35**	30
FeO	**7.34**	33	Bi	**15**	13
MnO	**0.97**	100	Cd	**1.5**	16
MgO	**0.16**	88	Ce	**97**	50
CaO	**0.37**	92	Cl	*30*	7
Na_2O	**0.33**	87	Co	**2**	44
K_2O	**7.72**	95	Cr	**56**	84
TiO_2	**0.05**	85	Cs	**260**	51
P_2O_5	**0.025**	57	Cu	**39**	60
H_2O+	1.46	24	Dy	**9.2**	23
H_2O-	**0.42**	23	Er	**6.7**	19
CO_2	*0.24*	8	Eu	**0.04**	19
F	**5.45**	35	F	**54500**	35
Li_2O	**2.43**	44	Ga	**99**	37
Rb_2O	**0.93**	75	Gd	**4.7**	23
Cs_2O	**0.028**	51	Hf	**9.7**	25
			Ho	**2**	22
	101.673		La	**30**	52
less O= F	2.3		Li	**24300**	44
			Lu	**2.2**	30
Subtotal	99.373		Mo	**4.3**	28
SnO_2	**0.165**	28	Nb	**198**	53
ZnO	**0.13**	82	Nd	**25**	37
TxOy	0.2	1469	Ni	**11**	54
			Pb	**80**	53
TOTAL	99.868	2673	Pr	**9.5**	24
			Rb	**8500**	75
Fe_2O_3 T	9.46	85	S	*300*	11
LOI	*2.3*	36	Sb	**4.2**	19
			Sc	**42**	46
			Sm	**6.6**	33
			Sn	**1300**	28
			Sr	**17**	64
			Ta	**82**	23
			Tb	**1.2**	27
			Th	**43**	46
			Tl	**34**	13
			Tm	**1.6**	19
			U	**20**	37
			V	**6**	38
			W	**320**	28
			Y	**33**	36
			Yb	**14**	36
			Zn	**1050**	82
			Zr	**82**	55

Note: All the major, minor and trace elements are recommended, except H_2O, CO_2, LOI, Cl and S.

N - Number of compiled data
TxOy - other trace elements as oxides

APPENDIX I. LIST OF CONTRIBUTING LABORATORIES

|001| Institut Fresenius, XFR-Labor, Hagenauer Street 15, 6200 Wiesbaden, Germany
|a| H.P. Schafer
|Codes| BFX, DFX

|002| CRB Analyse Service GmbH, Bahnhofstrasse 14, W-3414 Hardegsen, Germany
|a| W. Vogel, S. Pierdzig, E. Benner
|Codes| BFX, DFX

|003| MINTEK, Council for Mineral Technology, Private Bag X3015, Randburg 2125, South Africa
|a| E.J. Ring
|Codes| AAA, ASM, BFX
|Notes| SM, ICP-MS

|004| The Open University, Dept. of Earth Sciences, Walton Hall, Milton Keynes, MK7 6AA, GBR, England
|a| P. Potts, P. Webb, J. Watson
|Codes| BFX, DFX

|005| Centre de Recherches Archéologiques Médiévales, Université de Caen, F-14032 Caen Cedex, France
|a| D. Dufournier
|Codes| ASF, ASP, CCG, CCK, CCT, ECG
|Notes| SP, ICP-AES

|006| Johannes Gutenberg-Universität, Institut für Geowissenschaffen (FB 22), Saarstrasse 21, Postfach 3980, D-6500 Mainz, Germany
|a| K. Kritsotakis
|Codes| ASP, BSP, ECG
|Notes| SP, ICP-AES

|007| Anamet Services, St. Andrews Road, Avonmouth, Bristol BS11 9JP, England
|a| C.R. Jackson, J.C. Smith
|Codes| AAA

|008| The Univ. of Sheffield, Dept. of Earth Sciences, Beaumont Building, Brookhill, Sheffield S3 7HF, England
|a| R. Kanaris-Sotiriou
|Codes| BFX, DFX, ECG

|009| Institut für Mineralogie und Lagerstättenlehre, Techniche Hochschule, Susterfeldstrasse 22, D-5100 Aachen, Germany
|a| W.L. Plüger, G. Deissmann
|Codes| BFX, DFX, ECG

|010| COGEMA, Direction des Services et Filiales Minières, BP 71, 87250 Bessines/Barteme, France
|a| P. Tranquard
|Codes| AAA, ACT, ASP, ASP, CIC
|Notes| SP, ICP-AES

|011| Inst. de Investigaciones Electricas, Apartado Postal 475, Centro, Cuernavaca, Morelos 62000, Mexico
|a| G. Izquierdo
|Codes| BFX, ECG

|012| Inst. of Rock & Min. Analysis, Chinese Academy of Geological Sciences, 26 Baiwanzhuang Dajie, Beijing, P.R. CHINA
|a| Y. Ming
|Codes| AAA, ACT, ASM, ASP, BFX, BSM, BSP, CCG, CIS, CSM, CSP, DFX, ECG
|Notes| SM, ICP-MS; SP, ICP-AES

|013| Laboratory#013

|014| Techniche Universiteit, Interfaculty Reactor Institute, Mecklweg 15, 2629 JB Delft, The Netherlands
|a| F.M. Van Veen
|Codes| EMN

|015| Institute of Geological Experiment of Anhui Province, 47 Wuhu Road, Hefei, Anhui, P.R. China
|a| Sun Nai Kun
|Codes| ASF, BFX
|Notes| BFX, the results by BFX are in fact the mean of BFX and wet chemical Analysis.

|016| GEOCISA Geotecnia y Cimentos, Los Lianos de Jerez 10 y 12, Coslada 28820, Madrid, Spain
|a| C. Romero
|Codes| ASP, BSP
|Notes| SP, ICP-AES

|017| Earth Resources Center, University of Exeter, Laver Bld., North Park Road, Exeter EX4 4QE, England
|a| I. Stone
|Codes| BFX, DFX, ECG

|018| Universita di Padova, Dipt. di Min. e Petrologia, Corso Garibaldi 37; 35100 Padova, Italy
|a| G.P. De Vecchi
|Codes| AAA, ACT, CIS

Ringversuch ZINNWALDIT ZWC der GIT-IWG

Ergebnisse CRB Analyse Service GmbH

Element / Oxid	Meß-programm	Unit	Max.	Min.	**Mean**	RMS	RMS (rel.-%)	IWG-values
F	POWDER	Gew.-%	6,81	6,34	**6,59**	0,17	2,5	5,45
Na2O	OXIQUANT	Gew.-%	0,29	0,25	**0,27**	0,014	5,3	0,33
MgO	OXIQUANT	Gew.-%	0,18	0,16	**0,17**	0,008	4,8	0,16
Al2O3	OXIQUANT	Gew.-%	18,42	18,27	**18,33**	0,06	0,30	18,45
SiO2	OXIQUANT	Gew.-%	53,10	52,82	**52,97**	0,11	0,13	54,00
P2O5	OXIQUANT	Gew.-%	0,022	0,016	**0,020**	0,003	15	0,025
SO3	OXIQUANT	Gew.-%	0,056	0,042	**0,046**	0,006	12	0,045
Cl	POWDER	µg/g	49	24	**43**	10	24	30
K2O	OXIQUANT	Gew.-%	7,77	7,72	**7,75**	0,02	0,23	7,72
CaO	OXIQUANT	Gew.-%	0,37	0,36	**0,36**	0,002	0,56	0,37
Sc	OXIQUANT	µg/g	39	33	**35**	2	5,9	42
TiO2	OXIQUANT	Gew.-%	0,045	0,042	**0,043**	0,001	2,2	0,05
V	OXIQUANT	µg/g	8	1	**4**	2,3	54	6
Cr	OXIQUANT	µg/g	56	43	**47**	5	10	56
Mn	OXIQUANT	µg/g	7485	7436	**7459**	21	0,28	7500
Fe2O3	OXIQUANT	Gew.-%	9,29	9,23	**9,28**	0,03	0,27	9,46
Co	OXIQUANT	µg/g	21	0	**8**	7	95	2
Ni	OXIQUANT	µg/g	16	10	**12**	2	11	11
Cu	OXIQUANT	µg/g	61	35	**44**	9	20	39
Zn	OXIQUANT	µg/g	1033	1025	**1029**	3	0,33	1050
Ga	OXIQUANT	µg/g	105	103	**104**	1	0,80	99
Ge	POWDER	µg/g	2,9	1,7	**2,3**	0,3	14	
As	OXIQUANT	µg/g	42	18	**31**	8	26	31
Se	POWDER	µg/g	3,8	0,8	**2,5**	0,8	31	
Rb	OXIQUANT	µg/g	8466	8450	**8458**	7	0,08	8500
Sr	OXIQUANT	µg/g	23	15	**18**	3	17	17
Y	OXIQUANT	µg/g	68	59	**61**	4	5,9	33
Zr	OXIQUANT	µg/g	40	36	**39**	1	3,8	82
Nb	OXIQUANT	µg/g	196	193	**194**	1	0,46	198
Cd	POWDER	µg/g	3,4	0,1	**1,3**	1,4	57	1,5
Sn	POWDER	µg/g	1631	1565	**1592**	17	1,1	1300
Sb	POWDER	µg/g	4,7	0,4	**2,5**	1,0	41	4,2
Cs	POWDER	µg/g	262	245	**251**	4	1,6	260
Ba	OXIQUANT	µg/g	119	103	**112**	8	7,0	52
La	OXIQUANT	µg/g	42	24	**32**	6	20	30
Ce	OXIQUANT	µg/g	89	66	**74**	9	11	97
Pr	OXIQUANT	µg/g	5	0	**3**	2,5	96	9,5
Nd	OXIQUANT	µg/g	22	9	**16**	6	36	25
Sm	OXIQUANT	µg/g	4	0	**2**	1,5	90	6,6
Ta	POWDER	µg/g	69	62	**65**	2	3,1	82
W	POWDER	µg/g	336	308	**321**	7	2,2	320
Hg	POWDER	µg/g	1,6	1,4	**1,5**	0,1	5,4	
Pb	OXIQUANT	µg/g	109	104	**107**	2	1,6	80
Bi	POWDER	µg/g	25	20	**22**	1	5,4	15
U	OXIQUANT	µg/g	26	18	**24**	3	13	20