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Autor: Stern, W.B.

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Frau Prof. Dr. Emilie Jäger gewidmet

Preparation and cell refinement of mica microsamples

by *W. B. Stern*[1]

Abstract

Least squares refinement of X-ray powder diffractograms of mica microsamples is possible when preferred orientation is minimized electrostatically. Their relative 1-sigma errors for a, b, c and cell volume are 0.06, 0.04, 0.02 and 0.05% respectively. The correlation of a and b parameters is within the statistical error of data, but a, b versus c scatter far more. When literature cell parameters of pure end members muscovite-phengite-paragonite are combined in a triangular grid and used for a diffraction analysis of white 2M1-mica, the results obtained correspond trendwise only with chemical analyses performed on the same micas. One may conclude that even qualitative chemical analysis on microsamples (e.g. by energy-dispersive X-ray fluorescence) enables more reliable results than high-quality diffraction data. Though cell parameters a and b of white mica are certainly linked with "phengite"-, and c with "paragonite"-content, the interdependence seems to be more complex than expected from literature.

Keywords: 2M1-mica, cell refinement, X-ray diffraction, microsample, chemical composition.

Zusammenfassung

Zellverfeinerungen pulverdiffraktometrischer Aufnahmen von Mikroproben sind im Falle von Hellglimmer möglich, wenn Orientierungseffekte elektrostatisch reduziert werden. Typische 1-sigma-Relativfehler für a, b, c und Zellvolumen sind 0,06, 0,04, 0,02 und 0,05% für 2M1-Hellglimmer, von denen 53 unterschiedlicher Herkunft diffraktometrisch und röntgenfluoreszenzanalytisch untersucht worden sind. Werden aus der Literatur die b- und c-Zelldaten von Muskowit, Phengit und Paragonit in einem Dreiecksdiagramm kombiniert und zur diffraktometrischen «Analyse» von Hellglimmer verwendet, so zeigen die gefundenen Werte zwar eine ungefähre Korrelation mit den an denselben Proben erhobenen chemischen Daten; von einem quantitativen Zusammenhang kann aber – trotz der kleinen Relativfehler (XRD) – keine Rede sein. Offensichtlich sind die Beziehungen zwischen Gittergrösse und Chemismus komplexer, als z.B. durch die Bezeichnung «Phengit» zum Ausdruck kommt, bei dem Mg, Fe^{2+} und Fe^{3+} einen unterschiedlichen und wohl auch gegenläufigen Einfluss auf die a- und b-Parameter haben können.

Introduction

Lattice dimensions of crystals are essential parameters, but not easy to determine on low-symmetry flaky minerals like mica. When chemical data, based on bulk mineralogical (powdered) specimens are correlated with lattice parameters, the latter should be determined on powdered samples as well (not on single crystals), preferably on the same specimen, from which chemical information was obtained.

A recently developed preparation method for diffraction and chemical investigation on microsamples (HANDSCHIN, STERN, 1990) was tested by studying dioctahedral micas from schists, gneisses, granites and pegmatites of various origin.

Procedures and results

X-RAY DIFFRACTION (XRD)

When microsamples have to be investigated by X-ray diffraction or -fluorescence, the size of sample surface is important in order to get statistically relevant signals. Thus, 30 mg of powdered mica

[1] Mineralogisch-Petrographisches Institut der Universität, Bernoullistrasse 30, CH-4051 Basel.

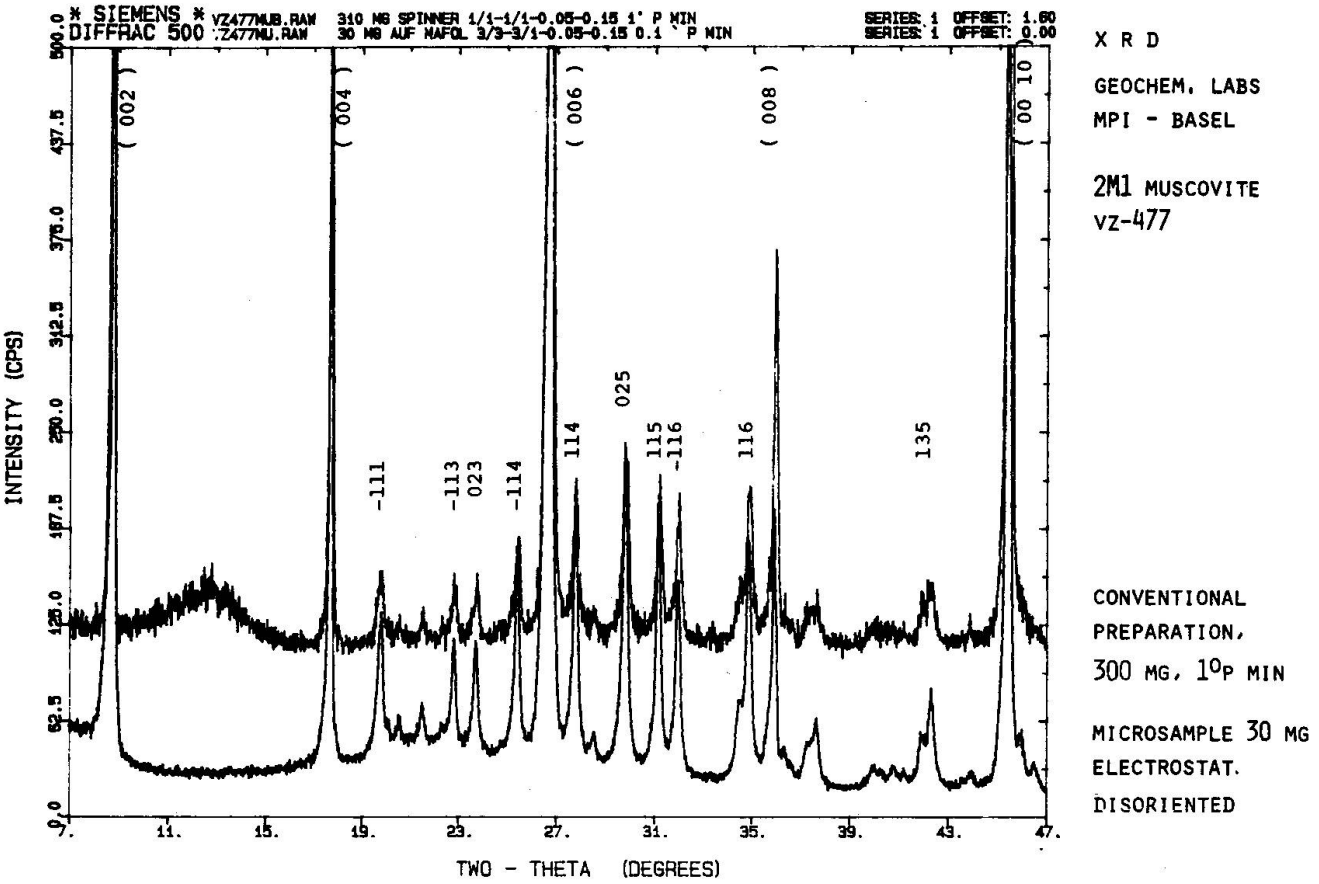

Fig. 1 X-ray diffraction pattern of powdered 2M1 – muscovite (Vz 477): Comparison between conventional preparation (300 mg in sample cup) and electrostatically disoriented microspecimen (30 mg) on stretched foil. Non-basal reflections of the disoriented microsample display double net intensities.

(10 mg would do as well for diffraction work) were distributed evenly on a stretched foil of 40 mm diameter, and fixed to it with 0.25 ml Griltex solution. In order to minimize preferred orientation, the mica flakes were disordered electrostatically by moving a plexiglass rod close to the surface of the drying mica / Griltex film.

In contrast to conventional mounting (e.g. 300 mg powdered mica in a sample cup or smear slides) not only basal spacings (00l) are prominent, but also random hkl-reflections (Fig. 1). Since least squares cell refinement (Appleman, Evans, 1973) of a monoclinic structure needs around 20 linearily independent strong reflections, it is evident that only disoriented samples can be used. Even these diffraction patterns may leed to plausible, but nevertheless erroneous cell parameters (Stern, 1987), when statistics of signal/peak ratios are not appropriate.

In order to combine suitable resolution and signal statistics, the samples were run with an angular goniometer speed of 0.1 degrees 2 Θ only (around 12 hours per exposure); least squares refinements were performed on-line after data reduction, the results transfered to a Lotus worksheet (reg. trade name LOTUS 1-2-3, version 3.0), (Fig. 2, Tab. 1). The statistical average errors are ± 0.003 Å for a, 0.004 for b and c, and 0.4 Å^3 for the cell volume respectively.

The correlation of a and b parameters is fair and corresponds to literature data, e.g. from Borg and Smith, 1969 (Fig. 2).

X-RAY FLUORESCENCE (XFA)

During the past few years a large amount of micas and "coexisting" mica pairs was re-examined with improved wavelength- and energy-dispersive X-ray fluorescence methods (WD-XFA, ED-XFA) for main constituents and trace elements, part of these unpublished data were used here to correlate them with XRD data.

Quantitative WD-XFA is still (Stern, 1979) executed on fused minerals for main element analysis, and on pressed powders for trace element analysis, both routines taking advantage of fully automated procedures optimized for intensity (matrix-) corrections. All data were automatically transferred to a Lotus worksheet file for further processing and graphical display.

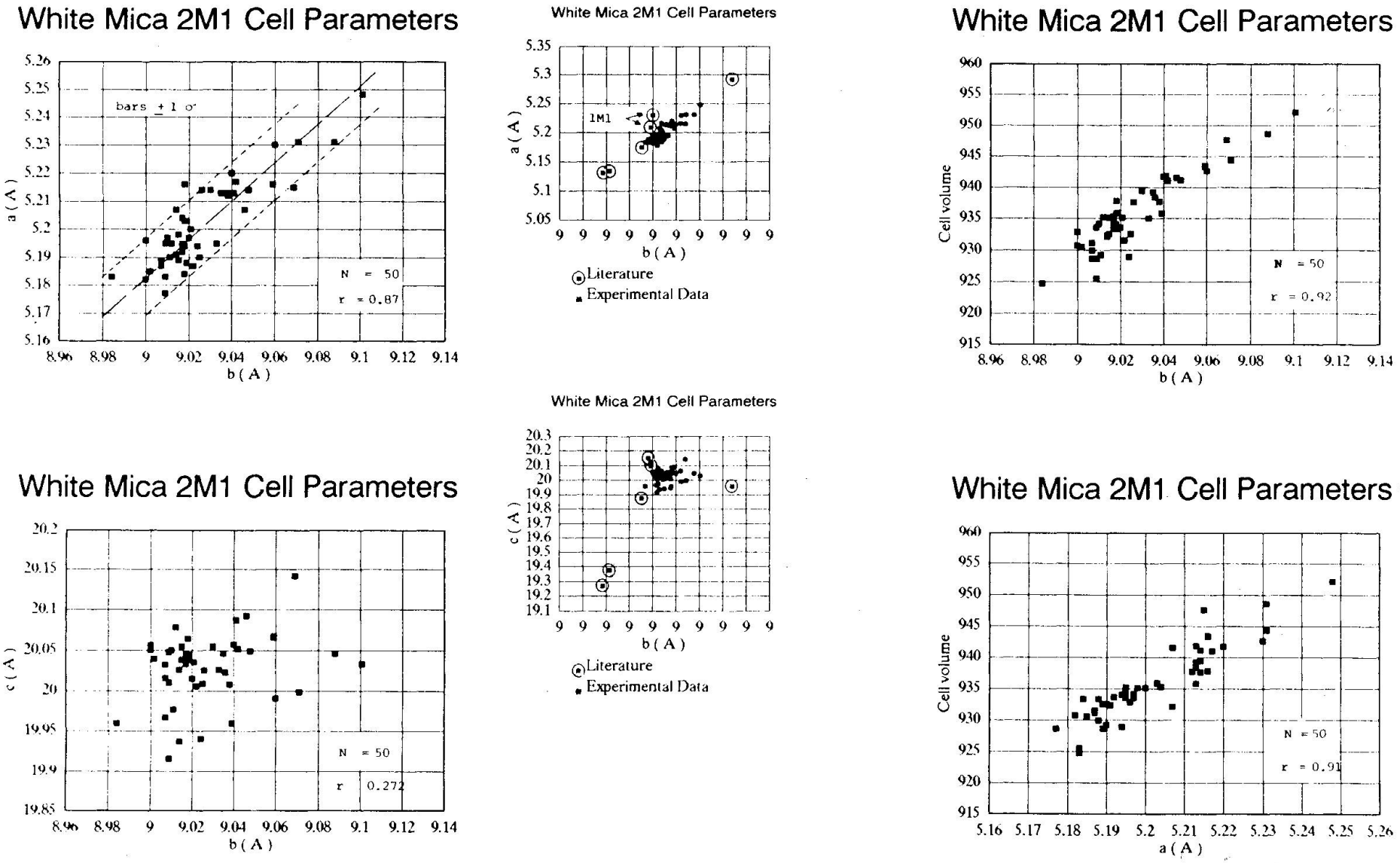

Fig. 2 Experimental X-ray powder diffraction data, and values from literature (for key see Fig. 4). Correlation of lattice parameters a versus b, and a, b versus cell volume are highly significant, in contrast to b versus c. Position and slope of the a versus b regression line corresponds well with data from literature (small inset). Note that 1M polytypes tend to plot outside the a/b correlational field of 2M1 white mica.

Tab. 1a Data White Micas (XRD) and selected chemical data (XFA).

2M1 Sample	Origin	Host	Grp	a (A)	error	b (A)	error	c (A)	error	beta	volume	Std. err.	Std. err.	log-ratios ex-XFA K/K.Ba	Si/Al	Al/Fe.	K/Rb	Fe/Mg	ED-XFA Fe203t	WD-XFA Fe203t	Specimen no.	Calculated (XFA) Pheng Si/Al %	Parag Na/Na+ %	Musc %
														HK=Oxide										
Ad41b	Bernardino	Sh	1	5.213	0.002	9.039	0.003	19.960	0.002	95.8	935.8	0.3	0.012	-0.051	0.236	0.610	*	0.14	3.88	4.10		40.1		59.9
Cal26	Calanca	Sh	1	5.200	0.002	9.021	0.002	20.035	0.001	95.8	935.1	0.3	0.012	-0.029	0.182	0.820	2.600	0.19	3.21	2.57	XV7361	27.0	4.6	68.5
Gli11	Bernardino	Gn	1	5.231	0.004	9.071	0.005	19.999	0.003	95.7	944.3	0.7	0.016	-0.009	0.255	0.446	2.120	0.41	7.15	7.08	XV7658	44.7	0.0	55.3
Ha225	Laengtal	Sh	1	5.190	0.003	9.011	0.004	19.977	0.006	95.9	929.2	0.5	0.019	-0.133	0.373	0.660	2.440	-0.02	2.39	2.69	XV7634	73.4	13.1	13.6
KAW0165	Eisten	Gn	1	5.230	0.003	9.060	0.004	19.991	0.003	95.7	942.6	0.5	0.015	-0.003	0.285	0.360	2.310	0.46	7.14	8.58	XV7642	52.0	0.7	47.3
Vals1	Vals	Gn	1	5.194	0.002	9.024	0.003	19.940	0.003	95.8	928.9	0.3	0.015	-0.046	0.265	0.569	*	0.15	4.50	4.10		47.1		52.9
Bedr107a	Bedretto	Gn	2	5.207	0.003	9.014	0.008	19.937	0.001	95.0	932.1	0.7	0.011	-0.013	0.247	0.580	2.520	0.36	4.65	5.29	XV7537	42.8	0.7	56.6
Blen49	Blenio	Sh	2	5.217	0.005	9.042	0.009	20.052	0.004	95.9	941.0	0.9	0.022	-0.010	0.138	0.951	2.554	0.34	2.51	2.66	XV7357	16.3		83.7
Ct22d	Levent	Gn	2	5.185	0.003	8.992	0.006	19.887	0.030	95.6	922.7	0.6	0.016	-0.076	0.093	1.410	2.590	0.05	0.81	0.82	XV7638	5.3	14.9	79.7
Gli04	Chiavenna	G	2	5.182	0.004	9.000	0.005	20.056	0.002	95.7	930.7	0.6	0.022	-0.010	0.128	1.180	2.210	0.46	1.68	1.79	XV7523	13.9	1.1	85.0
Hal99	Tosafall	Gn	2	5.213	0.001	9.036	0.003	20.023	0.001	95.7	938.4	0.4	0.015	-0.009	0.190	0.690	2.270	0.35	4.45	4.50	XV7345	28.9	7.8	63.3
KAW0160	Lebendun	Gn	2	5.212	0.002	9.038	0.004	20.008	0.002	95.8	937.7	0.4	0.017	-0.006	0.192	0.600	2.300	0.48	5.40	5.89	XV7615	29.4	0.7	69.9
KAW0207	Binntal	Gn	2	5.248	0.002	9.101	0.002	20.033	0.004	95.8	952.1	0.4	0.022	-0.008	0.275	0.420	1.960	0.46	7.19	7.68	XV7473	49.6	0.4	50.0
Hul132	Antigorio	Sh	3	5.189	0.003	9.007	0.004	19.967	0.001	95.7	928.6	0.5	0.012	-0.043	0.121	0.860	2.610	0.56	3.68	3.80	XV7549	12.2	7.6	80.2
HuSt900	Bavona	Gn	3	5.214	0.004	9.026	0.005	20.025	0.002	95.8	937.6	0.6	0.018	-0.022	0.233	1.036	2.310	0.36	2.76	4.40	IX1169	39.4	4.1	56.6
KAW0082	Croppo	Gn	3	5.214	0.003	9.048	0.011	20.049	0.002	95.8	941.1	0.9	0.018	-0.007	0.144	0.920	2.310	0.42	3.01	3.02	XV7646	17.7	1.6	80.7
KAW0083	Beura	Gn	3	5.216	0.004	9.018	0.005	20.040	0.001	95.8	937.8	0.5	0.016	-0.004	0.171	0.810	2.390	0.38	3.00	3.66	XV7630	24.3	0.3	75.4
Vz691	Verzasca	Sh	3	5.183	0.001	8.984	0.002	19.960	0.002	95.7	924.7	0.3	0.017	-0.410	0.110	1.175	2.660	-0.31	0.93	0.84	XV7674	9.5	3.8	86.7
Gli10	Prato	P	4	5.203	0.003	9.019	0.003	20.044	0.001	95.8	935.9	0.3	0.008	-0.018	0.142	0.804	2.464	0.67	4.07	4.45	XV7553	17.3	2.3	80.5
Vz297	Lavertezzo	P	4	5.195	0.001	9.009	0.002	20.048	0.001	95.8	933.5	0.2	0.016	-0.015	0.155	1.010	2.380	0.41	2.32	2.44	XV7506	20.4	2.3	77.3
Vz477	Odro	P	4	5.216	0.003	9.059	0.002	20.066	0.004	95.8	943.3	0.5	0.019	-0.008	0.159	0.700	1.760	0.87	6.56	6.20	XV7375	21.4	1.5	77.1
Vz501	Lavertezzo	P	4	5.187	0.001	9.007	0.001	20.032	0.001	95.8	931.1	0.2	0.011	-0.025	0.142	0.930	2.240	0.48	2.22	2.90	IX1163	17.3	5.5	77.2
WS62a	Morobbia	P	4	5.198	0.004	9.015	0.004	20.055	0.003	95.8	935.1	0.5	0.020	-0.014	0.126	1.156	2.640	0.37	1.79	1.79	XV7584	13.3	2.2	84.5
WS72b	Novate	G	4	5.185	0.002	9.002	0.003	20.039	0.002	95.7	930.5	0.3	0.014	-0.009	0.115	1.030	2.360	0.61	1.80	2.70	XV7603	10.7	1.2	88.1
81.200	Irkutsk	P	5	5.213	0.004	9.035	0.006	20.046	0.002	95.8	939.2	0.5	0.019	-0.032	0.117	0.950	2.370	0.17	1.83	2.35	XV4994	11.2	2.5	86.4
83.330	Rustum	P	5	5.190	0.003	9.025	0.002	20.009	0.002	95.8	932.5	0.4	0.015	-0.020	0.213	0.432	2.120	0.64	4.66	8.52	XV6367	34.5	4.0	61.5
86.321	Kali-b	P	5	5.196	0.003	9.000	0.003	20.051	0.001	95.8	932.8	0.4	0.011	-0.036	0.107	1.126	2.340	0.36	1.28	1.94	XV6290	8.7	6.9	84.3
86.323	Sharda	P	5	5.195	0.004	9.033	0.004	20.026	0.002	95.7	935.0	0.5	0.017	-0.030	0.149	0.782	1.530	0.63	2.68	4.11	XV6321	19.0	5.7	75.4
86.326	Badani	P	5	5.191	0.002	9.014	0.003	20.026	0.001	95.7	932.3	0.3	0.011	-0.021	0.117	0.985	1.629	0.49	2.56	2.81	XV6319	11.2	3.4	85.4
88.003gr	Morocco	P	5	5.184	0.002	9.018	0.003	20.064	0.003	95.8	933.3	0.4	0.017	-0.031	0.108	1.185	1.610	0.54	1.67	2.14	IX6542	9.0	5.9	85.1
88.005ru	Morocco	P	5	5.194	0.004	9.018	0.004	20.038	0.003	95.7	934.0	0.6	0.019	-0.031	0.128	0.936	1.840	0.41	2.88	3.35	IX6543	13.9	6.3	79.9
88.008	Argentina	P	5	5.204	0.002	9.017	0.001	20.033	0.002	95.8	935.3	0.3	0.015	-0.029	0.149	0.681	2.370	0.62	3.82	5.50	IX6541	19.0	5.7	75.4
88.010	Shivsh	P	5	5.195	0.003	9.017	0.003	20.046	0.004	95.8	934.3	0.3	0.011	-0.033	0.099	1.172	2.150	0.62	1.75	1.70	XV7084	6.8	1.7	91.5
89.001	Sitarama	P	5	5.197	0.001	9.020	0.003	20.015	0.002	95.8	933.5	0.2	0.012	-0.040	0.117	1.050	2.620	0.22	1.82	2.02	XV7265	11.2	4.4	84.4
89.003	Menakshi	P	5	5.187	0.002	9.022	0.004	20.006	0.002	95.8	931.5	0.4	0.017	-0.041	0.131	0.860	2.550	0.43	2.30	3.51	XV7267	14.6	2.6	82.9
89.005gr	PVSR-India	P	5	5.231	0.002	9.088	0.003	20.046	0.006	95.8	948.6	0.4	0.018	-0.008	0.174	0.532	2.160	0.79	6.47	7.90	XV7269	25.0	3.2	71.8
89.006	Vandana	P	5	5.195	0.004	9.012	0.005	20.078	0.004	95.8	935.2	0.6	0.019	-0.015	0.101	1.230	2.310	0.62	1.64	1.78	XV7271	7.3	3.0	89.7
90.009	Tucuman	P	5	5.216	0.003	9.059	0.011	20.067	0.004	95.8	943.4	0.9	0.028	-0.013	0.111	0.949	2.444	0.47	2.07	3.10	XV7703	9.7	4.3	86.0
90.010	Argentina	P	5	5.220	0.002	9.040	0.004	20.057	0.002	95.8	941.7	0.3	0.019	-0.010	0.075	0.982	2.465	0.50	1.80	3.13	XV7705	1.0	2.3	96.8
90.011	Zimbabwe	P	5	5.214	0.002	9.030	0.003	20.055	0.002	95.8	939.4	0.3	0.017	-0.010	0.064	1.059	2.137	0.87	2.81	3.10	XV7707	0.0		
89.009	Tanzania	P	5	5.215	0.004	9.069	0.014	20.141	0.009	95.9	947.6	1.6	0.038	-0.023	0.118	0.996	2.620	0.20	1.30	2.23	XV7085	11.4	2.2	86.4
Shilling	Sudan	P	5	5.177	0.003	9.009	0.006	20.010	0.003	95.7	928.6	0.7	0.019	-0.027	0.149	0.861	2.320	0.38	2.14	3.00	IX6532	19.0	5.1	76.0
086.010	Malaysia	G	6	5.197	0.002	9.010	0.005	20.050	0.005	95.8	934.1	0.6	0.020	-0.035	0.228	0.839	1.762	0.52		3.32	XV7305	38.2	4.5	57.3
094.004	Malaysia	G	6	5.213	0.002	9.041	0.003	20.087	0.005	95.8	941.8	0.3	0.015	-0.017	0.133	0.910	1.550	0.77	5.19	3.64	XV7307	15.1	3.1	81.8
094.008	Malaysia	G	6	5.207	0.001	9.046	0.006	20.092	0.004	95.8	941.5	0.3	0.020	-0.010	0.150	0.900	1.660	0.88	2.47	3.47	XV7309	19.2	1.4	79.4
094.009	Malaysia	G	6	5.188	0.001	9.019	0.005	20.045	0.003	95.7	933.3	0.5	0.023	-0.017	0.150	0.990	1.670	0.61	2.41	2.68	XV7311	19.2	2.1	78.7
094.010	Malaysia	G	6	5.203	0.002	9.018	0.003	20.044	0.001	95.8	935.8	0.3		-0.013	0.144	0.960	1.740	0.55	4.09	2.91	XV7313	17.7	2.1	80.2
094.014	Malaysia	G	6	5.189	0.001	9.015	0.003	20.038	0.004	95.8	932.5	0.1	0.014	-0.013	0.152	0.840	1.720	0.63	4.11	3.95	XV7317	19.7	1.4	79.0
094.015	Malaysia	G	6	5.192	0.002	9.017	0.003	20.045	0.003	95.8	933.6	0.4	0.013	-0.006	0.159	0.880	1.790	0.58	2.61	3.37	XV7317	21.4	0.8	77.8
103.001	Malaysia	G	6	5.188	0.003	9.007	0.007	20.016	0.011	95.8	929.9	0.8	0.033	-0.019	0.232	0.900	1.740	0.63	3.67	3.11	XV7321	39.1	2.9	58.0
Polytypes other than 2M1																								
KAW0041	Nalps	P	1	8.878	0.010	5.249	0.003	20.420	0.003	99.8	937.8	0.8	0.021	-0.007	0.134	1.110	2.450	0.64	1.98	2.30	XV7343		1.1	98.9
Vz690	Verzasca	Sh	3	5.169	0.005	8.991	0.003	10.145	0.003	97.9	467.0	0.5	0.007	-0.068	0.167	1.098	2.570	0.64	0.83		IX962		14.4	85.6

Tab. 1b Data White Micas (XRD) and selected chemical data (XFA).

Reproducibility test on one microsample (30 mg Rustum 83.330)

												Iter	Reflections used	Reflections rejected	Std.err.	Remarks
RUSTUM	A.Pradesh	P	5	5.190	0.003	9.025	0.002	20.009	0.002	95.79	932.5	0.4	4	20	2	0.015 sample position normal, 0.1'p min
RUSTUM2	A.Pradesh	P	5	5.205	0.003	9.027	0.002	20.019	0.002	95.75	935.8	0.5	5	25	1	0.013 removed from goniometer and re-positioned
RUSTUM3	A.Pradesh	P	5	5.212	0.002	9.036	0.003	20.019	0.002	95.82	937.9	0.4	4	27	1	0.014
RUSTUM4	A.Pradesh	P	5	5.207	0.003	9.026	0.005	20.016	0.002	95.75	936.1	0.5	4	25	1	0.015
RUSTUM5	A.Pradesh	P	5	5.203	0.004	9.023	0.005	20.023	0.002	95.79	935.2	0.7	8	30	2	0.021 goniometer speed 1'p min instead of 0.1
RUSTUM6	A.Pradesh	P	5	5.246	0.002	9.080	0.003	20.164	0.007	95.98	955.2	0.3	5	32	13	0.019 sample position too low, 0.5'p min
RUSTUM7	A.Pradesh	P	5	5.187	0.007	9.014	0.009	19.985	0.005	95.74	929.7	1.0	5	31	8	0.032 sample position too high, 0.5'p min
RUSTUM8	A.Pradesh	P	5	5.206	0.003	9.029	0.004	20.022	0.002	95.75	936.5	0.5	4	26	2	0.013 sample position normal, 0.1'p min
RUSTUM9	A.Pradesh	P	5	5.204	0.004	9.023	0.005	20.018	0.002	95.76	935.1	0.6	4	24	0	0.017
RUSTUM10	A.Pradesh	P	5	5.204	0.003	9.028	0.004	20.015	0.002	95.77	935.5	0.4	4	24	0	0.011
Average	N=10			5.206	0.003	9.031	0.004	20.029	0.003	95.79	937.0	0.53				
Std.dev.				0.015	0.001	0.017	0.002	0.0462	0.002	0.068	6.459	0.19				

Literature

B+S-1	Australia	P?	0	5.189		8.996		20.096			
B+S-2	A.Sponda	Sh	0	5.174		8.976		19.875			
B+S-4	A.Sponda	Sh	0	5.134		8.907		19.376			
B+S-5	California		0	5.211		9.038		19.947			
CHATT-Mu	synthet		0	5.188		8.990		20.152			
CHATT-Pg	synthet		0	5.130	0.001	8.893	0.002	19.270	0.003		
GUID-Mu	extrapol		0	5.183		8.994		20.123			
GUID-Ph	extrapol		0	5.291		9.169		19.960			
YOD-MuIM	synthet		0	5.208	0.010	8.995	0.020	10.275	0.005		
MOR-MuIM	Manitoba	P	0	5.230	0.020	9.000	0.020	10.072	0.005		

Host = Host rock type

G = Granite
Gn = Gneiss
Sh = Schist
P = Pegmatite

Grp =Main rock groups

1-4 Alpine
5 Precambrian
6 Triassic

* Data from SCHWANDER, et al., 1968

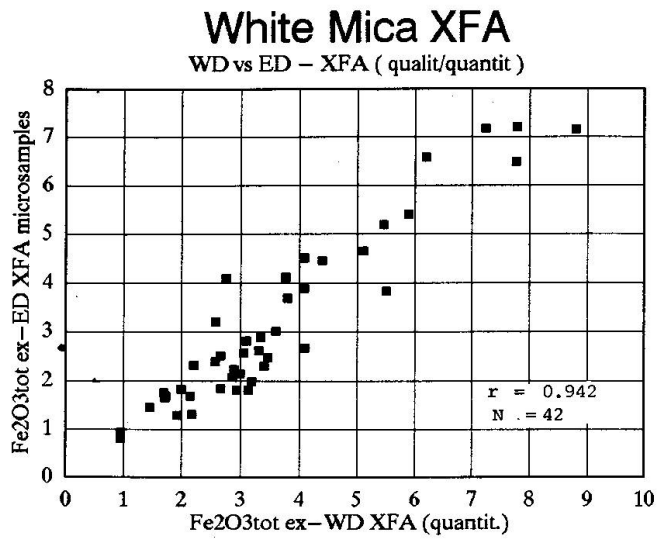

Fig. 3 Comparison of quantitative and qualitative X-ray fluorescence data (Fe_2O_3 total).
Qualitative: 30 mg powdered mica on stretched foil (as for x-ray diffraction), ED-XFA
Quantitative: fusion with $Li_2B_4O_7$ (Tab. 2), WD-XFA
The correlation coefficient (r = 0.942, N = 42) is better than the one obtained by phengite analysis XRD versus XFA.

Some microsamples which were examined by XRD were analyzed qualitatively by ED-XFA (STERN, 1985) in order to examine the reliability of this fast and efficient method of non-destructive simultaneous instrumental analysis (Fig. 3).

The analyzed mica concentrates cover a wide, though not the complete compositional field of di-octahedral mica. They represent various types of host rock, like Alpine schists, gneisses, granites and pegmatites, Triassic granites, and Pre-cambrian pegmatites from Argentina, India, Sudan and Tanzania.

Discussion

Cell parameters of white mica display a large variation, much larger than the error of data determination (ref., see Fig. 4):

	phengite	muscovite	paragonite
a	5.291	5.183	5.135
b	9.169	8.990	8.993
c	19.947	20.152	19.270

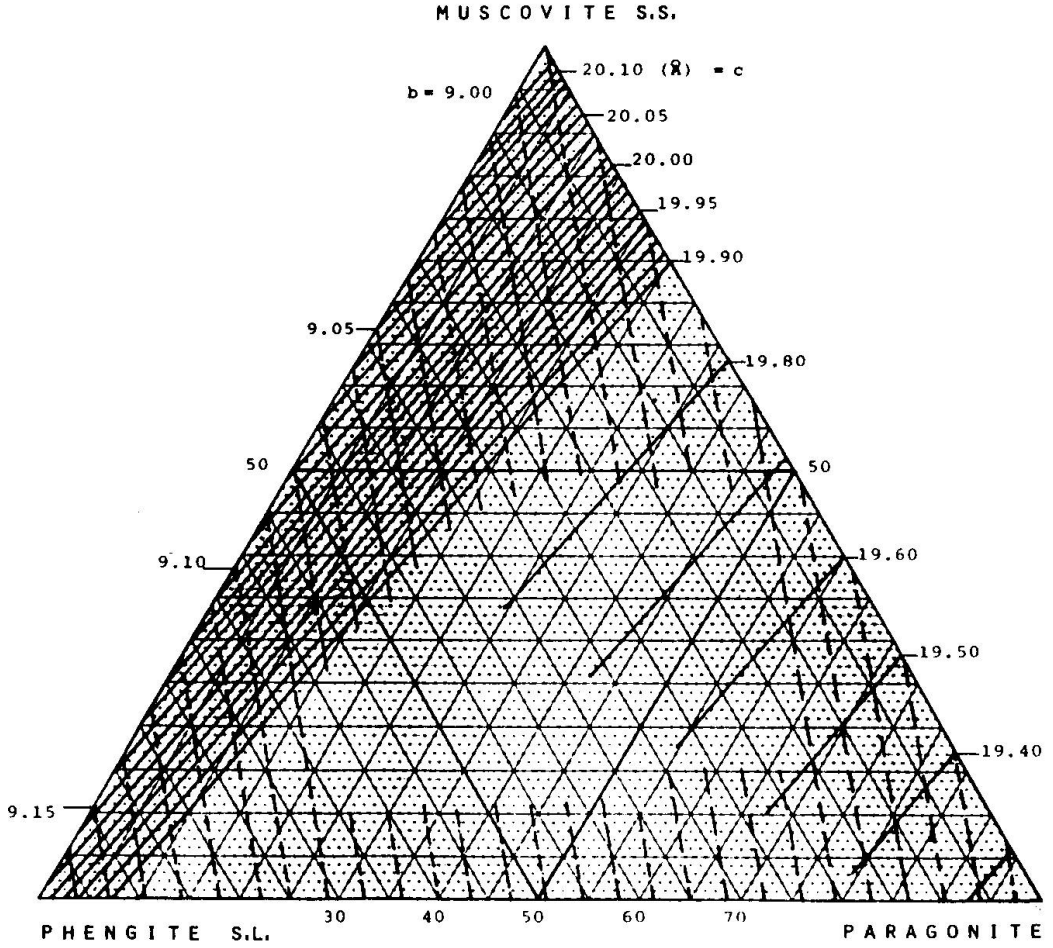

Fig. 4 Triangular plot of 2M1 dioctahedral micas muscovite – phengite – paragonite. Cell parameters b and c taken from literature: muscovite b, c after CHATTERJEE, JOHANNES, 1974; paragonite b, c after BORG and SMITH, 1969; phengite b after GUIDOTTI et al., 1989; phengite c after BORG and SMITH, 1969. The diagram enables – theoretically – the deduction of mica composition (% muscovite, paragonite, phengite) from experimentally determined cell parameters b and c. Far more reliable, and commonly used, is the direct chemical analysis.

The values for a and b have been correlated with the exchange of octahedral Al by Fe^{2+} and Mg combined with exchange of tetrahedral Al^{3+} by Si (Tschermak substitution, see e.g. GUIDOTTI et al., 1989). The value for c has been attributed to the exchange of interlayer K by Na (paragonite substitution, see e.g. CIPRIANI et al., 1968) – among other, less reported substitutions.

Corresponding correlation data published so far display a trendwise interdependence between diffraction and relevant chemical data, but the uncertainty of the correlation has been such that a quantitative use of b- or c-parameters for phengite or paragonite analysis seems hardly possible.

When b- and c-parameters of pure end members phengite, paragonite and muscovite (taken from literature) are combined in a triangular grid, it is – theoretically – possible to determine e.g. the phengite or paragonite content of an unknown white mica (Fig. 4). If results of such a procedure, however, are controlled by chemical analyses, the agreement of diffractometric and chemical data is not too encouraging:

	phengite		paragonite		muscovite s.s.		
	XRD	XFA	XRD	XFA	XRD	XFA	
Gli-04	8	14	7	1	85	85	(%)
Gli-11	19	45	20	0	61	65	
KAW-083	21	24	6	0	73	75	
KAW-160	29	29	8	1	63	70	
KAW-165	42	52	6	1	52	47	
KAW-207	60	50	0	0	40	50	
Vz-477	35	21	0	2	65	77	
WS-72b	10	11	6	1	84	88	

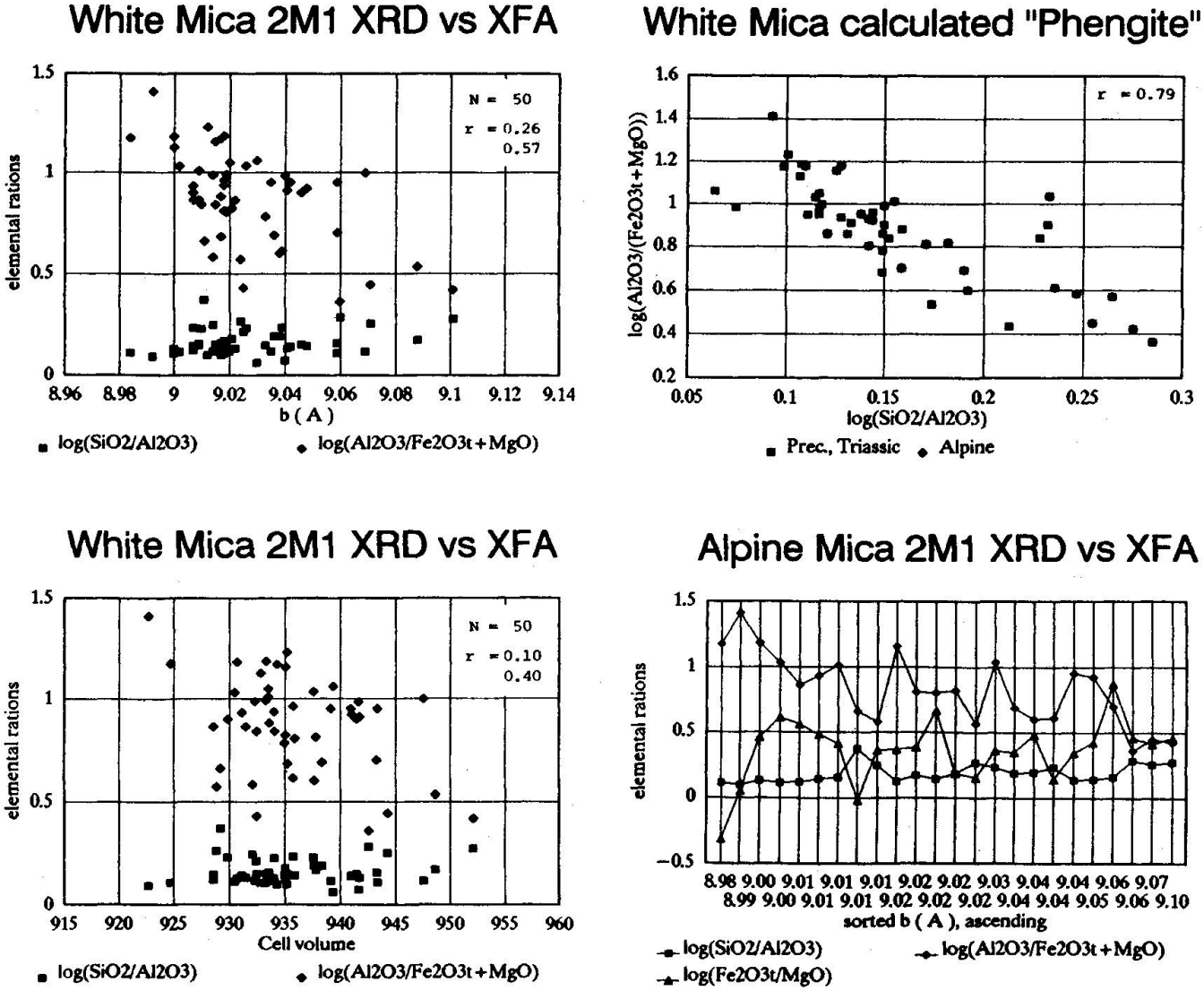

Fig. 5 Cell parameter b (XRD, experimental) and "phengite" content (XFA, experimental). Two elemental ratios are indicative, Si/Al connected with phengite content, and Al/Fe + Mg with ferrimuscovite and phengite content. Though a trendlike correlation between b and phengite content (XFA) exists, the interdependence is far too weak to be used for analytical purpose (i.e. phengite analysis by XRD).

The question arises (NAEF, STERN, 1982), whether lacking accuracy of diffractometrical cell determination has been the reason for this poor correlation, or the complexity of chemical substitutions occurring.

The present powder diffraction data on disoriented microsamples display relatively small errors, being obviously not the reason for the large scatter around a regression curve e.g. a versus c or b versus volume; the slope of the regression line, again, corresponds well with the situation expected from literature (BORG and SMITH, 1969).

The correlation found between cell data and relevant chemical data (Fig. 5) resembles much from what is known from the literature and is too weak to be used as a calibration function. Since it can not be explained by errors of measurement, opposite effects of chemical substitutions have to account for it. Certain assumptions have been too simple:

– phengite consists of at least two different species, ferro- and picrophengite; the effect of Fe^{2+} and Mg on a and b parameters probably being different (Fig. 5);

– ferric iron is always present and may influence a and b by either replacing tetrahedral or octahedral Al;

– interlayer Na is scarce in phengitic mica and therefore hardly responsible for large deviations of a and b (Fig. 6);

– the size of c certainly depends on the Na-content of mica but on eventual Ca, Ba, Rb as well, the latter often being neglected in chemical analysis, as is F whose influence on mica cell parameters is virtually unknown.

An intriguing fact is the obviously poor correlation of the c parameter with any of the chemical variables tested (Fig. 6). The use of basal spacings for paragonite quantification – as is common practice in petrographic literature – can therefore not be recommended. They are, however, helpful when paragonite has to be identified in presence of muscovite.

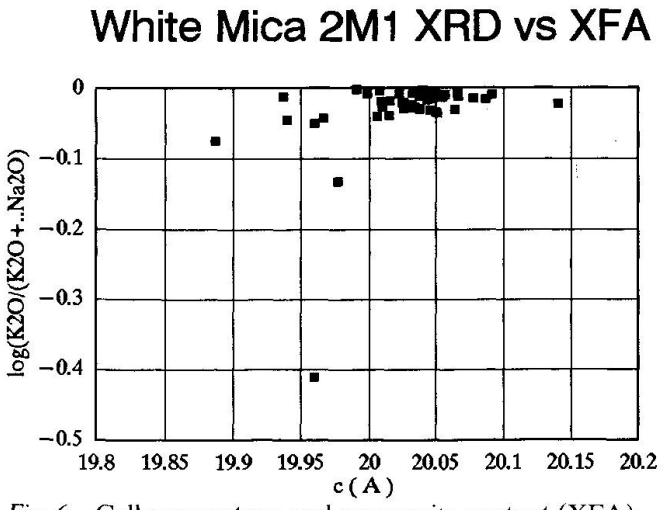

Fig. 6 Cell parameter c and paragonite content (XFA). Compositional variation of the paragonite content is 0 to 25%, main part of points plotting between 0 and 10% paragonite. No correlation between paragonite percentage and cell parameter c is statistically ascertained (Alpine muscovites s.l. N = 23, r = 0.50; Precambrian, Triassic muscovites s.l. N = 19, r = 0.15).

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Appendix: Instrumental conditions

A. X-ray diffraction (XRD)

apparatus	D-500, Siemens GFR
excitation	Cu 40 kV, 30 mA, no primary filter, secondary graphite monochromator
apertures	automatic divergence slit set at 3, 3–3 entrance aperture, 1–0.05–0.15 secondary side
exposure	0.1 2 Θ P min., angular increment 0.02 2 Θ angular limits 3–73 2 Θ
software	DIFFRAC-500 least squares refinement after APPLEMAN, EVANS, 1973, 3 basal reflections pre-indexed, minimum error for rejection 0.05 20; only reflections > 10 cps were taken for refinement, low scaling factor of 0.1 for reflections below 20 2 Θ
specimen	30 mg powdered mica on Makrofol (KG, Bayer) foil 40 mm ø electrostatically disoriented (HANDSCHIN, STERN, 1990)

B. X-ray fluorescence (XFA); wavelength-dispersive (WD-XFA)

apparatus	SRS-303, Siemens GFR
excitation	Rh-end window tube, variable according to chemical element; 40 to 60 kV, 70 to 40 mA, 10 to 100 sec
analyzers	In Sb for Si, P, S, Cl multilayer OVO-55 for Al, Mg, Na, F LiF for K- and L-lines of heavy elements fitted background correction for traces
software	SPECTRA/AT (Siemens) routines QUANTXV, QUANTIX data management with LOTUS 1–2–3
specimen	main constituents: fused glass beads consisting of 150 mg ignited sample powder + 2350 mg $Li_2B_4O_7$ annealing in 95 Pt–5 Au crucible, diameter 32 mm, inductive furnace (STERN, 1979); trace elements: 800 mg dried sample powder pressed into Al-rings, diameter 20 mm, elvacite binder

energy-dispersive (ED-XFA)

apparatus	Spectrace-5000, Tracor X-ray, U.S.A.
excitation	W-tube (127 microns Be window), 6 to 50 kV, 0.35 to 0.20 mA, integration time per procedure 200 sec, dead time kept below 40%
analyzer	solid state detector (Li)–Si, with ultrathin Be-window, 7.6 microns
software	Tracor X-ray, running on IBM AT 80-311 314 Mb, 2 Mb RAM
specimen	30 mg on stretched Makrofol foil, as described under section XRD