## **GEOCHEMISTRY** =

## A Unique Record of *P*–*T* History of High-Grade Polymetamorphism

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As has been shown in recent publications [1, 2], the Precambrian granulite complexes repeatedly affected by high-temperature polymetamorphism (HTM) retain records of thermal and dynamic history of both events. Repeated high-grade metamorphism should apparently create a new isotopic system that determines the age of rock, whereas the older mineral assemblage should be replaced by a new one that fits the younger thermodynamic parameters, the more so as the repeated metamorphism is realized along ductile deformation zones [3]. However, the relicts of the first event are retained within these zones, and the age difference of the events may reach hundreds of million years. Hence, the repeated HTM occurred rapidly, and the complete reequilibration of minerals was not achieved.

The metapelite sample taken from 30 km west of the Bakklykraal structure [3] located in the Central Zone of the Limpopo Complex (Alldays district, South Africa) yielded a unique mineral assemblage that retained a complete record of both deformation stages (D) and the corresponding metamorphic cycles (M), i.e., D2/M2 (~2.65 Ga) and D3/M3 (~2.0 Ga) [4, 5]. The metapelite is composed of garnet (Grt), cordierite (Crd), orthopyroxene (Opx), quartz (Qtz), biotite (Bt), spinel (Spl), sapphirine (Sap), and plagioclase (Pl). Zircon rutile, titanite, and apatite are accessory minerals. Muscovite (Ms) and chlorite (Chl) are secondary low-temperature minerals. The granoblastic texture of the massive rock

shows no distinct leucosome. The metapelite shows three distinct microstructural mineral assemblages: (i) porphyroblasts of  $Grt_1$ ,  $Crd_2$ ,  $Opx_2$ , and Qtz (Figs. 1a, 1b); (ii) reaction texture (Figs. 1c, 1d)

$$Grt_1 + Qtz = >Crd_2 + Opx_2$$
(1)

and (iii) complete replacement of  $Grt_1$  with  $Crd_2$  that contains oriented Opx<sub>2</sub> lamellas and oblong grains of the newly formed garnet (Figs.1e, 1f). The reaction texture is typical [8]: Opx<sub>2</sub> symplectites around Grt<sub>1</sub> grains in the Crd<sub>2</sub> matrix are surrounded by a narrow Pl rim and a thick outer  $Opx_2$  rim that formed contemporaneously. The BSE images in Fig. 1 suggest three stages of polymetamorphic evolution of this unique sample: decompression cooling (DC1), nearly isobaric heating (IH), and the second decompression cooling (DC2). Events D2/M2 and D3/M3 in the Alldays district have been dated with isotopic methods [3, 5]. Therefore, we can suggest that stage DC1 corresponds to the first event (~2.65 Ga), whereas stages IH and DC2 correspond to the second event (~2.0 Ga). This interpretation is corroborated by complete disappearance of Grt<sub>1</sub> in some places of the rock (stage IH), formation of Grt<sub>2</sub> (DC2), systematic variation of mineral compositions at each stage of the rock evolution, and development of the integrated P-T path.

The *chemical zoning* was studied with microprobe profiling. Local microanalyses of minerals were carried out for all three types of microtextures (Fig. 1). The results are distinguished by the Mg index ( $X_{Mg} = Mg/(Mg + Fe)$  of minerals and partly by the Al content in Opx (Table 1). All minerals related to stage DC1 are zonal:  $X_{Mg}^{Grt_1}$  decreases from centers of porphyroblasts (0.553) to their margins (0.46–0.44). During formation of reaction texture (1) at stage IH,  $X_{Mg}^{Grt_1}$  varies from 0.46 to 0.42. At stage DC2,  $X_{Mg}^{Grt_2}$  decreases to 0.34.

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**Fig. 1.** Proceeding of reaction (1) in metapelite T66 from the Central Zone of the Limpopo Granulite Complex, South Africa. (a) The oldest garnet and cordierite porphyroblasts with a fragmentary reaction rim; Crd–Opx symplectite and Opx rim arise at paths of metamorphic fluid percolation; (b) orthopyroxene porphyroblast that does not take part in formation of the reaction texture; (c, d) gradual replacement of garnet according to reaction (1) and expansion of corona texture; (e) complete replacement of garnet by reaction texture with retention of its morphology; (f) newly formed garnet within the recrystallized corona. BSE images.

Compo- nent	Porphyroblasts (cores)				Corona texture				Recrystallized symplectite			Sma
	Grt1	Crd <sub>1</sub>	Opı <sub>1</sub>	Bt <sub>1</sub>	Grt <sub>1</sub>	Crd <sub>2</sub>	Opı <sub>2</sub>	Bt <sub>2</sub>	Grt <sub>2</sub>	Crd <sub>3</sub>	Opı <sub>3</sub>	Spr
SiO <sub>2</sub>	39.80	49.24	52.12	36.63	38.68	49.76	50.94	37.77	37.83	49.22	50.38	12.37
TiO <sub>2</sub>	0.00	0.00	0.20	5.64	0.10	0.00	0.20	4.48	0.12	0.06	0.22	0.07
$Al_2O_3$	21.94	33.18	4.74	16.65	21.72	34.35	5.52	16.76	21.43	32.45	5.83	61.37
$Cr_2O_3$	0.04	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.27	0.00	0.78	0.63
FeO	21.86	2.55	16.98	12.96	26.39	3.47	20.13	11.26	28.32	3.90	18.75	7.31
MnO	0.28	0.07	0.30	0.40	0.34	0.00	0.30	0.30	0.83	0.08	0.21	0.00
MgO	14.74	12.15	26.51	15.83	10.49	12.05	22.60	16.55	8.80	11.13	22.80	15.84
CaO	0.50	0.03	0.00	0.20	1.79	0.00	0.10	0.00	1.98	0.05	0.13	0.04
Na <sub>2</sub> O	0.09	0.00	0.10	0.20	0.00	0.10	0.20	0.20	0.00	0.11	0.28	0.00
K <sub>2</sub> O	0.00	0.02	0.00	8.41	0.00	0.12	0.00	9.89	0.00	0.01	0.14	0.04
Total	99.25	97.29	100.95	96.92	99.52	99.85	99.98	97.22	99.57	97.01	99.52	97.67
		Proportions of cations										
Si	2.993	4.992	1.873	5.312	2.979	4.938	1.875	5.441	2.962	5.035	1.858	1.509
Ti	0.000	0.000	0.005	0.615	0.006	0.000	0.006	0.485	0.007	0.005	0.006	0.006
Al	1.945	3.964	0.201	2.846	1.972	4.017	0.239	2.845	1.967	3.911	0.253	8.819
Cr	0.002	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.017	0.000	0.023	0.061
Fe <sup>#</sup>	1.375	0.216	0.510	1.571	1.699	0.288	0.619	1.356	1.845	0.333	0.578	0.745
Mn	0.018	0.006	0.009	0.049	0.022	0.000	0.009	0.037	0.055	0.007	0.007	0.000
Mg	1.653	1.835	1.419	3.420	1.203	1.782	1.239	3.551	1.022	1.696	1.254	2.878
Ca	0.040	0.003	0.000	0.031	0.148	0.000	0.004	0.000	0.165	0.005	0.005	0.005
Na	0.013	0.000	0.007	0.056	0.000	0.019	0.014	0.056	0.000	0.022	0.020	0.000
Κ	0.000	0.003	0.000	1.555	0.000	0.011	0.000	1.817	0.000	0.001	0.007	0.006
Total	8.040	11.023	4.025	15.456	8.029	11.055	4.005	15.588	8.040	11.015	4.011	14.029
X <sub>Mg</sub>	0.553	0.895	0.736	0.685	0.415	0.861	0.667	0.780	0.3556	0.836	0.694	0.794

Table 1. Representative microprobe analyses of minerals from metapelite T66

Of course, it is practically impossible to rigorously record the composite parameters of each stage change due to the superimposed diffusion of Fe and Mg and equivocal microtextural effects of reaction (1). The zoning of  $Crd_2$  and  $Opx_2$  in a symplectitic texture serves as a more reliable criterion (Fig. 2): the  $X_{Mg}$  value of these phases decreases from the  $Grt_1$  margin (indication of *T* growth) and then increases (*T* fall) [9]. We performed more than 250 analyses, and the results obtained allowed us to trace the *P*–*T* evolution of the studied metapelite sample.

The P-T paths at each stage of evolution were deduced using the method described in [2]. For the Bt + Grt + Crd assemblage, the temperature was estimated with two independent thermometers and the pressure was calculated from local reaction (1) if both temperature data turned out to be close to each other. Table 2 presents the summary estimates of P-T parameters of local equilibria, and Fig. 3 shows the generalized P-T path. This path consists of three segments that correspond to DC1 (1), IH (2) and DC2 (3). As was mentioned above, the transitions between the different stages are slightly overlapped. However, the trends outlined from microtextures of rocks and zoning of minerals are unequivocally supported by the integrated P-T path. A low-angle positive slope of segment 2 extending along the garnet isopleth remains somewhat problematic (in theoretical terms, this segment must be isobaric). On the one hand, this is caused by the impossibility of strictly estimating the garnet composition at the final stage of development of the reaction texture at the end of stage IH. On the other hand, this stage is controlled by the growth of Grt<sub>2</sub> with  $X_{Mg} = 0.42-0.34$ .

The results obtained have shown that Korzhinsky's principle of local equilibrium combined with microstructural analysis and thermobarometric estimates

Grt <sub>1</sub>		Crd		Opx			Bt		<i>T</i> , °C*		P, kbar	
No.	X <sub>Mg</sub>	X <sub>Ca</sub>	Nº	X <sub>Mg</sub>	Nº	X <sub>Mg</sub>	a <sub>OK</sub>	N⁰	X <sub>Mg</sub>	Crd-Grt	Bt-Grt*	GCOQ**
Porphyroblasts												
265	0.553	0.013	248	0.863	208	0.702	0.072			815		8.1
266	0.525	0.012	251	0.851	211	0.679	0.057			807		7.6
263	0.526	0.016	215	0.855	210	0.684	0.065			798		7.6
264	0.541	0.013	232	0.863	209	0.690	0.066			796		7.9
257	0.512	0.010	213	0.848	240	0.670	0.042			795		7.3
1	0.505	0.028	107	0.850	85	0.653	0.052			780		7.4
22	0.500	0.019	107	0.850	86	0.653	0.057	31	0.701	773	793	7.4
270	0.503	0.018	215	0.851	201	0.663	0.031			773		7.1
259	0.490	0.069	285	0.873	228	0.659	0.037			760		6.9
2	0.491	0.019	108	0.856	84	0.670	0.054			744		6.9
62	0.491	0.026	108	0.856	59	0.679	0.043			743		6.8
60	0.490	0.042	108	0.856	20	0.679	0.048			741		6.7
3	0.485	0.014	106	0.854	83	0.661	0.058	18	0.713	740	758	6.9
61	0.480	0.031	108	0.856	83	0.661	0.043			728		6.7
23	0.480	0.014	108	0.856	19	0.678	0.051			728		6.6
4	0.478	0.017	108	0.856	82	0.653	0.048			726		6.8
7	0.443	0.012	35	0.843	79	0.675	0.062	18	0.713	707	711	5.9
5	0.456	0.012	106	0.854	81	0.664	0.051			701		6.2
6	0.450	0.012	108	0.856	80	0.662	0.057			689		6.1
8	0.441	0.020	29a	0.861	78	0.681	0.058			664		5.7
9	0.432	0.017	71	0.872	77	0.699	0.061	74	0.780	627	621	5.4
	I	I	I	I	S y r	'nplecti	tes		I	I	I	I
9a	0.421	0.022	29	0.873	29	0.667	0.055			616		5.4
9a	0.421	0.022	10	0.871	10	0.684	0.052			620		5.2
9a	0.421	0.022	19	0.859	19	0.678	0.051			646		5.3
9	0.432	0.017	29a	0.861	56	0.663	0.049			648		5.5
9	0.432	0.017	30	0.861	29a	0.696	0.047			655		5.3
9a	0.421	0.022	33	0.849	30	0.666	0.058			655		5.7
9	0.432	0.017	15	0.852	105	0.740	0.056	75	0.724	665	678	4.9
51	0.432	0.048	13	0.850	33	0.650	0.063			668		5.7
9a	0.421	0.022	35	0.843	15	0.660	0.058			675		5.8
9	0.432	0.017	11	0.848	13	0.657	0.061			678		5.8
9a	0.421	0.022	14	0.841	34	0.659	0.055			681		5.5
9	0.460	0.043	32	0.857	11	0.661	0.054			684		5.7
9a	0.421	0.022	16	0.832	14	0.656	0.061			687		5.6
9	0.432	0.017	20	0.838	66	0.696	0.047			695		5.9
51	0.432	0.048	31	0.835	31	0.661	0.063	220	0.701	704	708	5.7
274	0.455	0.033	289	0.843	16	0.654	0.062			705		5.7
291	0.465	0.033	290	0.844	18	0.671	0.057	243	0.713	705	700	5.7
27	0.425	0.046	31	0.835	31	0.661	0.063			713		5.9
101	0.424	0.042	102	0.850	281	0.689	0.075	284	0.712	724	727	6.1
49	0.423	0.042	32	0.857	280	0.694	0.066	282	0.712	737	737	6.3
Symplectites with Grt <sub>2</sub>												
275	0.443	0.010	216	0.835	202	0.658	0.035	<i>.</i> .	0 6	704		5.7
249	0.412	0.046	242	0.829	229	0.679	0.045	34	0.690	696	706	5.1
246	0.394	0.055	253	0.834	241	0.655	0.048			665		5.0
226	0.356	0.054	242	0.829	204	0.651	0.065			626		4.2
225	0.343	0.052	253	0.834	241	0.655	0.048			601		3.8

Table 2. Compositions of minerals in the Grt + Crd + Opx + Qtz assemblage and P-T parameters of their local equilibria at water activity of 0.2

(\*) Temperature was calculated with Crd–Grt and Bt–Grt geotermometers [6] (uncertainties are 11°C and 16°C, respectively). (\*\*) Pressure was calculated with the Grt–Crd–Opx–Qtz barometer [7] (uncertainty is 0.5 kbar).

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**Fig. 2.** Typical chemical zoning of the  $Opx_2$ -Crd<sub>2</sub> symplectite as a product of reaction (1). Points of minimums on curves in Fig. 2a correspond to the change of IH by DC2.

makes it possible to reconstruct a very detailed history of polymetamorphic granulite–facies complexes using a particular sample witness.

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**Fig. 3.** Generalized P-T path of polymetamorphic evolution of sample T66 from the Central Zone of the Limpopo Granulite Complex, South Africa. (1) DC1 segment (~2.65 Ga), (2) nearly isobaric heating (IH), and (3) subsequent stage DC2; (2) and (3) correspond to the isotopic age of ~2.0 Ga [4].

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