Chlorite of hydrothermal origin in the Strzelin and Borów granites (Fore-Sudetic Block, Poland)

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Chlorite, a product of very low- to low-grade metamorphism, is frequently used as a geothermometer because of the fact that its structure and chemical composition can reflect the physical and chemical conditions of its formation. In the hydrothermally altered Strzelin and Borów granites (the Fore-Sudetic Block, Poland) chlorite is ubiquitous. It is found in two forms: spherulitic and post-biotite, and was formed in different ways in different parts of the Strzelin and Borów granites: as result of (1) replacement of biotite or (2) crystallisation from fluid. The chlorite formed in the Borów granite shows a higher Fe content than that in the Strzelin granite, a feature related to the content of Mg and Fe in the host rock. Temperatures of chlorite formation are the lowest for unaltered granite and then gradually increase for slightly, moderately and strongly altered granite and are the highest in hydrothermal veins. This means that the temperature of the hydrothermal fluid was higher than that of the altered granitic bodies. Moreover, the spherulitic chlorite formed at a higher temperature than did the post-biotite chlorite, and is usually smaller because biotite replacement lasted longer than did the crystallisation of spherulitic chlorite directly from hydrothermal fluid. Such patterns are likely to occur in other granitic bodies.

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INTRODUCTION

Chlorite can crystallise in a number of different environments. It is a ubiquitous product of very low- to low-grade metamorphism influencing a great variety of rocks of different formation age such as in Cambrian basaltic vesicular lavas (Lopez-Munguira *et al*., 2002), Late Jurassic shallow-marine sandstones (Ryan and Hillier, 2002) and early Oligocene sandstones and greywackes with andesitic volcanic clasts (Schmidt and Livi, 1999). It is also one of the most abundant and widespread alteration products in geo- or hydrothermal environments such as in the Neogene Kuroko Cu-Pb-Zn vein-type deposits of Japan (Shikazono and Kawahata, 1987), in quartz/carbonate hydrothermal veins in amphibolites and gneisses of the Sobotín region and pegmatites of the Žulová and the Strzegom–Sobótka massifs (Zimák, 1999), in Cretaceous granitic rocks at Ashio (Hamasaki *et al*., 1995) and Variscan granitic massifs of the Karkonosze (Wilamowski, 2002; Kozłowski and Marcinowska, 2007) and Strzelin areas (Ciesielczuk and Janeczek, 2004; Kozłowski and Marcinowska, 2007).

Chlorite group displays a wide range of chemical composition, which can vary depending on the conditions of formation (e.g., Cathelineau and Nieva, 1985; Bailey, 1988; Cathelineau, 1988; Battaglia, 1999; Schmidt and Livi, 1999; Krzemiński, 2000; Zimák, 1999; Vidal *et al*., 2005; Plissart and Féménias, 2009). A general crystallochemical formula of chlorite can be given as follows (de Caritat *et al*., 1993):

$$(R_u^{2+} R_y^{3+} \square_z)^{VI} (Si_{4-x} Al_x)^{IV} O_{10+w} (OH)_{8-w}$$

where: $u + y + z = 6$, $z = (y - w - x)/2$, w frequently reaches zero, R^{2+} usually represents Mg^{2+} or Fe^{2+}, R^{3+} typically represents Al^{3+} or Fe^{3+}, and $\square$ represents structural vacancies. Superscripts VI and IV denote octahedral and tetrahedral occupancy, respectively.

The main factor which controls chlorite formation in either metamorphic or hydrothermal processes is temperature, and so a number of attempts at using chlorite as a geothermometer have been made. However, chlorite geothermometry was criticized, even discredited, by Jiang *et al*. (1994). What is more, Frey and Robinson (1999) warned against using the chlorite geothermometer as a function of its chemical composition, par-

ticularly for chlorites formed at low temperatures. According to them this is only possible for homogeneous phases formed in conditions of thermodynamic equilibrium. Nevertheless, the application of chemical composition of chlorite as a geothermometer has not been abandoned (Walshe, 1986; Merriman *et al*., 1995; Zang and Fyfe, 1995; Xie *et al*., 1997; Zang *et al.*, 1997; Zimák, 1999; Krzemiński, 2000; Vidal *et al*., 2001, 2005; Plissart and Féménias, 2009), though is approached with considerable caution. Also, Parra *et al*. (2005) experimentally showed that the Si-content of chlorite is sensitive to temperature for the various divariant assemblages. Chlorite geothermometry has been modified, as by Battaglia (1999), for example, who exploit X-ray diffraction patterns in chlorite to this end, and by Inoue *et al*. (2009). Given the usefulness of geothermometers in geology, this ubiquitous mineral provides a simple and easy means of establishing conditions of the host rock formation.

This paper describes the characteristics of chlorite formed during the hydrothermal alteration of granitoids from two Variscan granitic massifs: the Strzelin and the Strzegom–Sobótka massifs, in the Fore-Sudetic Block of SW Poland. These two localities were chosen because of the varied patterns of alteration of the host rock: (1) gradational, as in the Strzelin granite, and (2) complex, as in the shear zone cropping out in the Borów quarry within the Strzegom–Sobótka granite. Also, some comments on the application of the chlorite geothermometer are made.

GEOLOGICAL SETTING AND PETROGRAPHY

The Strzelin granite builds the northern part of the Strzelin Massif. Petrographically it is fine-grained biotite granite accompanied by more leucocratic medium-grained biotite granite (Borkowska, 1956; Bereś, 1969). The age of the Strzelin granite was established by the $^{87}Rb/\ ^{86}Sr$ method as 347 ±12 Ma (Oberc-Dziedzic *et al*., 1996). Moreover, Oberc-Dziedzic *et al*. (1996), and Oberc-Dziedzic (1999, 2007) distinguished dykes of younger (330 ±6 Ma), light biotite-muscovite granite within the biotite granite. Hydrothermal alteration of the Strzelin granite resulted in the formation of mineralised veins and subsequent alteration of the surrounding granite, the effects being seen in a large active quarry located east of the city of Strzelin. Based on the content of biotite, spherulitic and post-biotite chlorite and the kind and amount of other hydrothermal minerals, three stages of alteration of the Strzelin granite around hydrothermal veins have been distinguished: (1) slightly altered granite, (2) moderately altered granite and (3) strongly altered granite. Strongly altered granite lacks biotite and is usually depleted in quartz. Albite and microcline are the only feldspars. Hydrothermal minerals such as spherulitic chlorite, prehnite, clinozoisite, laumontite, calcite, and muscovite are abundant. This granite facies is usually bleached. The slightly altered granite differs from the unaltered one in the prevalence of post-biotite chlorite over biotite and in the presence of scarce minute hydrothermal minerals such as albite, spherulitic chlorite, titanite and prehnite. In the moderately altered granite almost all of the biotite is replaced by chlorite, while the feldspars are also altered. Hydrothermal minerals are found in large

quantities. The size of hydrothermal minerals increases with the degree of alteration and the mineral assemblage changes with depth (Ciesielczuk, 2000*b*; Ciesielczuk and Janeczek, 2004; Ciesielczuk, 2007).

The granite cropping out in the Borów quarry is part of a biotite-hornblende granite (Puziewicz, 1990), and is called the Strzegom granite (Majerowicz, 1972), or a granite of the Kostrza type (Kural and Morawski, 1968). It is part of the Strzegom–Sobótka Variscan granitoid massif. Its age was established by the Rb-Sr method for 325–330 Ma (Pin *et al*., 1989) and by means of the Pb-Pb zircon method as 303 ±2 Ma (Turniak *et al*., 2005). Specimens containing hydrothermal chlorite were collected from the large (approximately 80 m) shear zone exposed in the northern wall of the Borów 17 quarry. This zone is cut by many hydrothermal subvertical veins, mostly of E–W strike, filled mainly with quartz. Granite in this zone is strongly altered with metre-scale variations (Ciesielczuk, 2000*a*). A specimen of unaltered, medium-grained granite was collected next to the shear zone and consists of plagioclase, microcline, quartz and biotite, with accessory titanite, zircon and apatite. The altered Borów granite contains albite and/or microcline, quartz, chlorite and pyrite. Minute amounts of muscovite, prehnite, titanite, zircon and apatite were also found.

Chlorite in both locations is of hydrothermal origin, but the effect of hydrothermal alteration varies (Ciesielczuk, 2002). Alteration in the Strzelin granite produced an abundance of hydrothermal minerals and is gradational and restricted to a few centimetre-wide (on average) zones around veins and fractures whereas in the Borów granite the entire granite in the shear zone is strongly altered, though its mineralogical composition is simple.

ANALYTICAL METHODS

More than one hundred samples of altered and unaltered Strzelin and Borów granites were collected in the field. Subsequently thin sections were prepared of representative samples: 21 from the Strzelin granite and 17 from the Borów granite and examined by standard polarizing microscope. Then, selected chlorite grains from unaltered and altered granites and hydrothermal veins were examined by means of scanning electron microscopy (SEM) *JSM 35C* (University of Silesia, Poland) and *Jeol-JSM 5410* (Jagiellonian University, Poland). Additionally, fragments of hydrothermal vein fillings were prepared and viewed by SEM in environmental mode to observe the habits and succession of minerals formed in the hydrothermal veins.

The chemical composition of the chlorite was determined by means of electron microprobes: *Superprobe JCXA-733*, U = 15 kV, I = 15 nA (the Mineralogical Institute of Russian Academy of Science, Russia); SEM *JEOL JSM-35* with *LINK QX2000* (the Department of Earth Sciences, Keele University, UK); *Superprobe JEOL 8600* (Geological Institute, Aarhus University, Denmark); and *Cameca SX100*, U = 15 kV, I = 10 nA, beam size 1mm (Faculty of Geology, Warsaw University). Altogether 258 analyses of chlorite composition in 180 grains were conducted.

Mineral phases were analysed using X-ray diffraction using a *Geigerflex Rigaku Denki*, CoKα radiation with Fe filter, $U = 30$ kV, $I = 25$ mA, tl = 2 s, ss = 0.02° (University of Silesia, Poland). The presence of interstratifications or intergrowths within the chlorite crystals was investigated in two ways: (1) using *Philips CM 20* high-resolution transmission electron microscopy (HRTEM) operated at 200 kV with lattice image 1.4 Å, and (2) by XRD, chlorite from the vein in the Strzelin granite being separated, then powdered, oriented, glycolated and heated to 180°C and to 550°C for 2 hours.

FORMS OF CHLORITE

Chlorite in the granites investigated occurs in post-biotite and spherulitic forms (Figs. 1 and 2). The post-biotite chlorite, forming as a result of partial or entire replacement of the biotite, is termed a secondary hydrothermal mineral. The size of grains ranges from 0.1 to 1.5 mm (Fig. 2A, B, D–F). The localisation of particular types of chlorite within the granite depends on its origin.

Spherulitic chlorite forms smaller (*ca*. 0.05 mm), radiant crystals. It crystallised in two possible ways:
– crystallisation from hydrothermal fluid in fractures, microfractures or intergranular spaces in granite as a primary hydrothermal mineral (Figs. 1 and 2C);
– replacement of post-biotite chlorite as a secondary hydrothermal mineral (Fig. 2D–F).

According to Janeczek (1983) this alteration consists in the dissolving of post-biotite chlorite and its recrystallisation in the presence of crystal nuclei.

Both types of chlorite optically show pale green to creamy pleochroism and characteristic, subnormal, greyish-blue interference colours. Pleochroic colours of chlorites formed in the Borów granite are darker (green) than these from the Strzelin granite.

SITES AND FREQUENCY OF CHLORITE WITHIN GRANITE

Post-biotite chlorite is present even in unaltered granite. The process of replacement of biotite has been widely described (Veblen and Ferry, 1983; Olives-Baños and Amouric, 1984; Eggleton and Banfield, 1985; Parneix and Petit, 1991; Janeczek, 1994; Ciesielczuk, 2000*b*). The Strzelin granite contains up to a few per cent of chlorite, whereas the Borów granite contains less than 1%.

Post-biotite chlorite is frequently found in the slightly altered Strzelin granite. In moderately altered granite its content decreases, while the content of spherulitic chlorite increases. It hardly ever occurs in strongly altered granites. Spherulitic chlorite is almost absent in unaltered granites. It is frequent in moderately and strongly altered ones, except in the bleached zones which surround hydrothermal veins. The width of these zones is approximately 0.5 cm and the degree of alteration is high, but chlorite is almost absent there.

Spherulitic chlorite is also frequent in hydrothermal veins. The fracture filling of the Strzelin granite is mainly polymineralic, where chlorite and quartz are the prevalent minerals. In the sequence of crystallisation chlorite crystallises at relatively high temperatures as the fourth mineral after quartz, feldspars and muscovite, and before clinozoisite, prehnite, laumontite/kaolinite and calcite (Ciesielczuk and Janeczek, 2004).
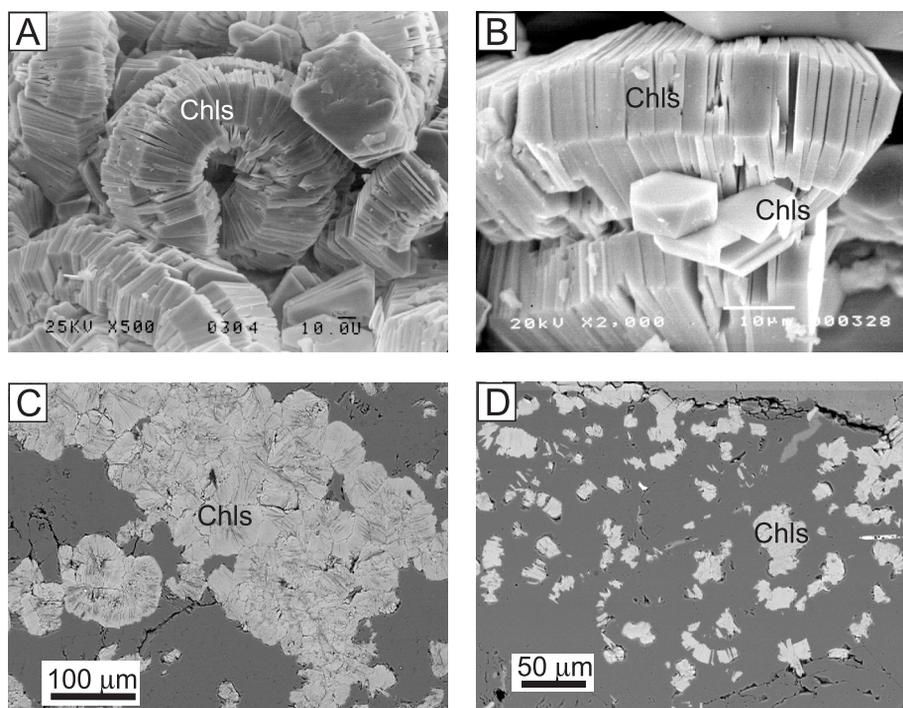

Fig. 1. Aggregates of spherulitic chlorite (Chls) present in hydrothermal veins in the Strzelin granite (A, B) and strongly altered Borów granite (C, D)
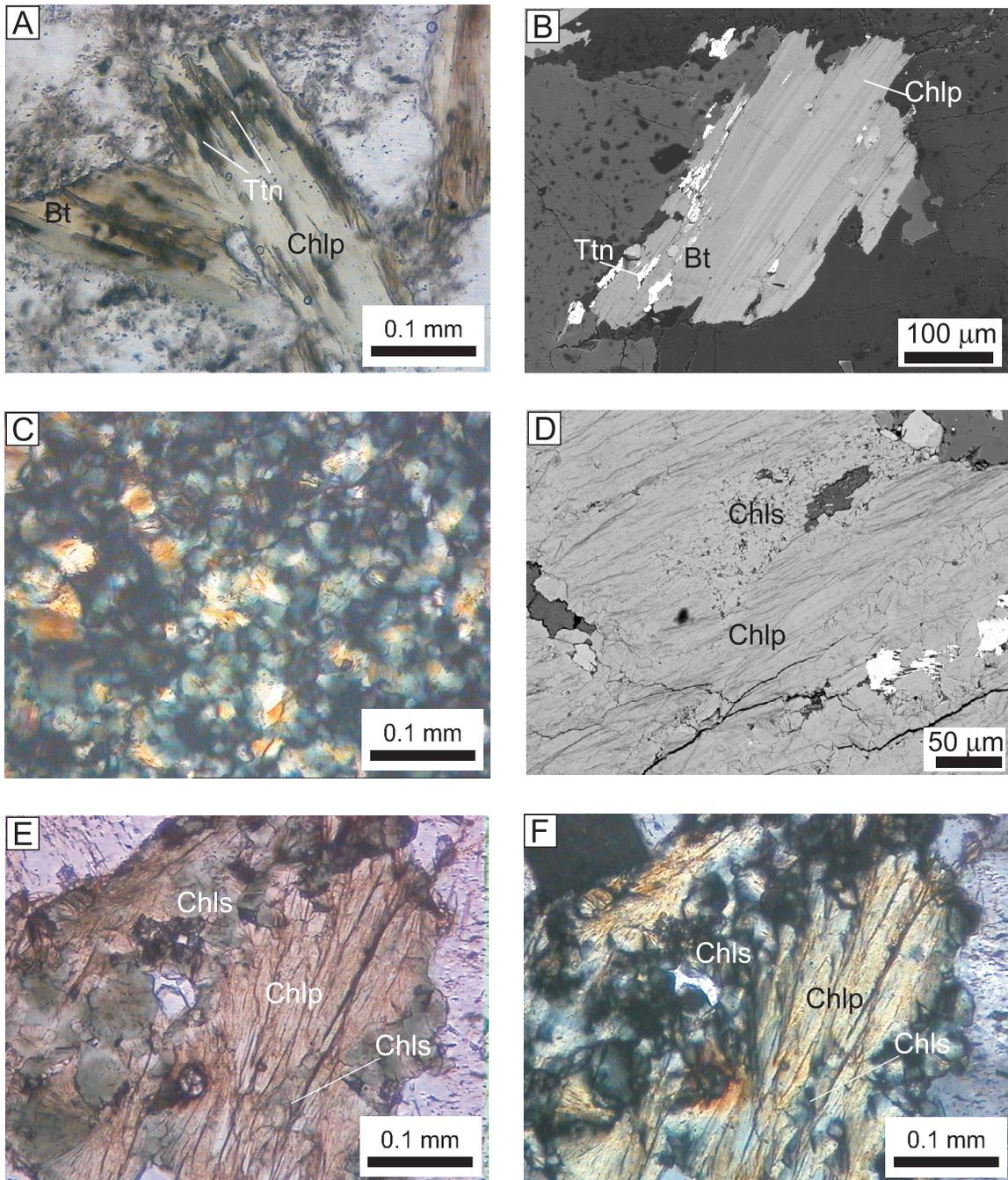
SEM images

Fig. 2A, B – replacement of biotite (Bt) by post-biotite chlorite (Chlp), titanite (Ttn) seen in fracture planes; C – spherulitic chlorite; D–F – the replacement of post-biotite chlorite (Chlp) by spherulitic chlorite (Chls); the process of replacement starts along the grain boundaries and fracture planes

A, C, E, F – optical microscope images, A, E – plane polarized light; C, F – crossed polars; B, D – BSE images; A – strongly altered Strzelin granite; B – slightly altered Strzelin granite; C–F – strongly altered Borów granite

The hydrothermal veins in the Borów granite are mainly monomineralic, filled with quartz. Only certain narrow, wide veins up to 1 cm are polymineralic and consist of quartz, feldspars, spherulitic chlorite and fluorite.

CHEMICAL COMPOSITION OF CHLORITE

The chemical composition of the chlorite is shown on the chlorite classification diagram recommended by the Nomenclature Committee of the AIPEA (Bailey, 1980; Fig. 3). Chlorite grains from the Strzelin granite contain 67% of chamosite particles (cha) $(Fe_5^{2+}Al)(Si_3Al)O_{10}(OH)_8$, 31% of clinochlore (cli) $(Mg_5Al)(Si_3Al)O_{10}(OH)_8$ and 1% of pennantite (pen) $(Mn_5^{2+}Al)(Si_3Al)O_{10}(OH)_8$ on average. Chlorite grains formed in unaltered granite contain 60–70% cha, 29–39% cli and 1–2% pen, chlorite grains from slightly altered granite contain 60–79% cha, 20–38% cli and 1–2% pen, and chlorites from strongly altered granite contain 61–73% cha, 25–37% cli and 1–3% pen. The composition of chlorites
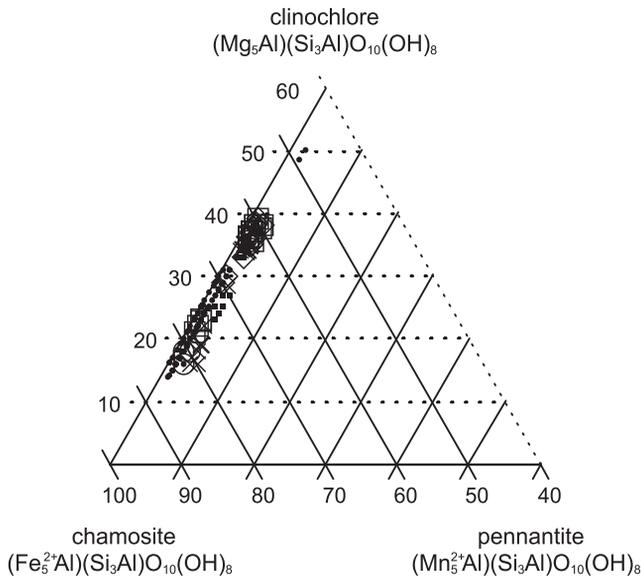
Fig. 3. Chemical composition of chlorites plotted on the clinochlore–pennantite–chamosite diagram

Chlorite from the Borów granite: unaltered (open circles), strongly altered (filled circles), and from the Strzelin granite: unaltered (open diamond), slightly altered (open square), strongly altered (filled square) and hydrothermal vein (cross)

formed in hydrothermal veins of the Strzelin granite ranges from 63 to 65% cha, from 34 to 35% cli and from 1 to 2% pen (Fig. 3). Chlorites from the Borów granite contain less magnesium but more iron, 76% of chamosite, 23% of clinochlore and 1% of pennantite on average. Chlorites formed in unaltered granite contain 80–82% cha, 16–18% cli and 1–2% pen, chlorites from the strongly altered granite contain 48–86% cha, 14–20% cli and 0–2% pen, chlorites formed in hydrothermal veins range from 63 to 64% cha, from 34 to 35% cli and from 1 to 2% pen (Fig. 3).

Microprobe analyses of chlorite of different shapes and formed in different parts of the Strzelin granite are shown in Table 1. Data in the first four columns show the variability of chlorite composition in the altered Strzelin granite up to the hydrothermal vein. The Al^{IV} content increases towards the mineralisation zone (1.25, 1.28, 1.29 and 1.36 a.p.h.f.u. respectively). The next two columns show a similar average composition of the core and rim parts of chlorite grains, and the last two columns give the composition of post-biotite and spherulitic chlorite formed within the Strzelin granite. Microprobe analyses of chlorite of different shapes and formed in different parts of the Borów granite are shown in Table 2. Since hydrothermal alteration in the shear zone in Borów was multistadial and complex, progressive alteration has not been observed. The various averaged chemical compositions of chlorite grains in five macroscopically and microscopically different samples of strongly altered Borów granite is shown in columns 2–6 and the mean value is given in column 7. Chlorite crystallised in hydrothermal veins contains the highest Fe_{tot} and Al^{IV} content. The chemical compositions of cores and rims of chlorite grains are

also similar to those of chlorites of post-biotite and spherulitic forms. Chlorites from the Borów granite are more ferrugineous than those from the Strzelin granite. These data are consistent with the results of research of Janeczek (1983, 1985) in the Strzegom–Sobótka Massif. This author observed a similar chemical composition of all chlorites present in pegmatites and granitoids in different parts of the massif.

Major cation relationships in the chlorite grains investigated are shown in Figure 4. The relationship between Fe and Mg shows a simple linear correlation with a negative slope and a correlation coefficient of 0.80 (Fig. 4A). But there is no correlation between Mg content with respect to Al^{IV} or Al^{VI} (Fig. 4B, C) and Al^{IV} *versus* Al^{VI} (Fig. 4D).

The ratio Fe/(Fe+Mg) in all the grains of chlorite investigated is relatively high, and ranges from 0.64 to 0.70 for the Strzelin granite and from 0.68 to 0.84 for the Borów granite. The $Al^{IV}/(Si+Al^{IV})$ ratio ranges from 0.30 to 0.35 for the Strzelin granite and from 0.29 to 0.34 for the Borów granite (Tables 1 and 2; Fig. 5; Ciesielczuk, 2000b). The relations of the tetrahedral Al to Si: $Al^{IV}/(Si+Al^{IV})$ *versus* octahedral sheet composition expressed by Fe/(Fe+Mg) in chlorite grains investigated is shown in Figure 5. All points are grouped more or less together and these points do not show any mutual dependence.

PURITY OF CHLORITE

The presence of intergrown phases within chlorite sheets was postulated by Olives-Baños and Amouric (1984), Jiang *et al.* (1994), Xu and Veblen (1996) and other authors. Chlorite can be contaminated by kaolinite or interstratified with berthierine or smectite, which eliminates the mineral composition as a basis for geothermometer calculation.

In the cases examined presence of smectite can be neglected as the sum of $CaO + Na_2O + K_2O$ in all analyses is lower than 0.3 wt.%. Moreover, Table 3 shows XRD data for chlorite formed in the hydrothermal vein and the strongly altered Strzelin granite. The XRD patterns are almost identical, and match the chamosite Ib pattern (ASTM 13-0029). For the purpose of detection of chlorite in the hydrothermal vein the sample was (1) sedimented, oriented, air-dried, (2) glycolated and (3) heated to 180°C for 2 hours and (4) to 550°C for 2 hours (Fig. 6). After saturation of the chlorite with ethylene glycol the 14.15 Å peak (001) stayed at the same position, which means, that there are no swelling interlayers. Heated to 180°C the chlorite sample faded, but the peak positions stayed the same. The sample of chlorite heated to 550°C turned brownish and peak positions and intensities changed. The (001) peak moved to 13.98 Å with maximum intensity, which means that the hydroxyl group was removed from the chlorite structure. This chlorite treatment demonstrated the absence of mixed layer minerals involving swelling phases, so it can be concluded that the chlorite is pure at the detection level of the XRD method.

Hence, high-resolution transmission electron microscopy (HRTEM) was applied. The post-biotite chlorite from unaltered and slightly altered Strzelin granite shows no signs of the

Averaged microprobe analyses of chlorite formed in the Strzelin granite, structural formulae calculated on the basis of 14O, and values of chlorite formation temperatures calculated on the basis of the Cathelineau (1988) and the Kranidiotis and MacLean (1987) methods

Chlorite location/shape	Unaltered granite	Slightly altered granite	Strongly altered granite	Hydrothermal vein	Rim	Core	Post-biotite chlorite	Spherulitic chlorite
Number of analyses	9	34	29	21	17	15	25	17
SiO_2	25.25	24.60	24.80	24.23	24.67	24.70	24.75	24.11
TiO_2	0.04	0.14	0.10	0.02	0.11	0.12	0.08	0.03
Al_2O_3	21.08	19.74	20.42	21.51	19.97	20.06	20.31	21.83
FeO_{tot}	31.49	34.88	32.52	31.86	33.91	33.53	32.54	32.99
MnO	0.81	0.60	0.86	0.78	0.66	0.69	0.67	0.90
MgO	10.43	8.27	9.47	9.66	8.81	9.13	9.61	9.04
Cr_2O_3	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.01
NiO	0.02	0.03	0.01	0.04	0.03	0.01	0.02	0.05
CaO	0.11	0.06	0.10	0.17	0.07	0.06	0.12	0.14
Na_2O	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02
K_2O	0.02	0.09	0.01	0.00	0.04	0.07	0.05	0.00
H_2O	11.00	10.83	10.95	11.01	10.88	10.92	10.95	10.96
Total	99.08	99.26	99.26	99.31	99.18	99.33	99.13	100.06
cha %	63	70	65	64	68	66	65	66
cli %	36	29	33	34	31	33	34	32
pen %	1	1	2	2	1	1	1	2
Si	2.75	2.72	2.70	2.64	2.72	2.71	2.71	2.60
Al^{IV}	1.25	1.28	1.29	1.36	1.28	1.29	1.29	1.40
Site T	4	4	4	4	4	4	4	4
Al^{VI}	1.30	1.30	1.33	1.40	1.31	1.31	1.33	1.38
Ti	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00
Fe_{tot}	2.87	3.24	2.99	2.90	3.13	3.08	2.98	3.05
Mn	0.07	0.06	0.08	0.07	0.06	0.06	0.06	0.08
Mg	1.69	1.36	1.54	1.57	1.44	1.49	1.57	1.46
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.02
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
K	0.00	0.01	0.00	0.00	0.01	0.01	0.01	0.00
Site O	5.97	5.99	5.97	5.98	5.98	5.98	5.98	6.00
Fe/(Fe+Mg)	0.63	0.70	0.66	0.65	0.68	0.67	0.66	0.68
$Al^{IV}/(Si+Al^{IV})$	0.31	0.32	0.32	0.34	0.32	0.32	0.32	0.35
T [^oC][1]	**334**	**349**	**355**	**376**	**351**	**352**	**354**	**388**
T [^oC][2]	**326**	**341**	**342**	**355**	**340**	**341**	**340**	**364**

tot – total iron content as FeO; nd – not determined; [1] – temperature calculated on the basis of the Cathelineau (1988) method; [2] – temperature calculated on the basis of the Kranidiotis and MacLean (1987) method

presence of interstratification or intergrowths of other minerals within the chlorite crystals (Fig. 7).

RELATIONSHIP BETWEEN CHLORITE AND ROCK COMPOSITION

Xie *et al*. (1997) showed a high correlation between the MgO content in chlorite and that in the host rock. Cathelineau and Nieva (1985) and Shikazono and Kawahata (1987) suggested that the iron and magnesium content in chlorite depends on the iron and magnesium content in the host, unaltered rock.

On the diagrams of MgO/FeO in chlorite *versus* MgO/FeO in unaltered rock, created on the basis of examples derived from volcanic rocks from different localities, all points lie close to a 1:1 line. A few points outside this line were interpreted as the effect of the influence of additional factors, such as the MgO/FeO content of hydrothermal fluid.

The MgO content in the unaltered Strzelin granite is 0.7% (Bereś, 1969) or 0.8% (Ciesielczuk, 2000b). The Borów granite contains 0.47, 0.63% (Majerowicz, 1972) and 0.19% (Ciesielczuk, 2000b) of MgO. This means that the MgO content in the Strzelin granite is slightly higher than that in the Borów granite. A similar relationship was found for the MgO content in

Averaged microprobe analyses of chlorite formed in the Borów granite, structural formulae calculated on the basis of 14O, and values of chlorite formation temperatures calculated on the basis of the Cathelineau (1988) and the Kranidiotis and MacLean (1987) methods

Chlorite location/shape	Unal-tered granite	Strongly altered 835	Strongly altered 833	Strongly altered 846/5	Strongly altered 838	Strongly altered 842	Strongly altered average	Hydro-thermal vein	Rim	Core	Post-biotite chlorite	Spherulitic chlorite
Number of analyses	8	14	21	29	39	22	125	12	24	25	64	46
SiO_2	24.05	25.57	24.73	23.40	24.55	24.76	24.60	22.92	24.92	24.72	24.45	24.30
TiO_2	0.04	0.04	0.04	0.04	0.03	0.26	0.08	0.04	0.04	0.05	0.04	0.04
Al_2O_3	18.49	17.98	19.27	19.18	19.25	18.84	18.91	19.75	19.14	18.90	19.55	19.50
FeO_{tot}	40.01	34.91	37.18	40.59	37.56	38.64	37.78	41.11	35.83	36.61	36.48	36.73
MnO	0.74	0.39	0.40	0.33	0.29	0.26	0.34	0.33	0.42	0.44	0.44	0.44
MgO	5.09	9.41	6.76	4.94	6.37	5.28	6.55	4.37	7.82	7.74	7.21	7.19
Cr_2O_3	nd	0.01	0.01	0.01	0.02	nd	0.01	0.02	0.02	0.01	0.01	0.01
NiO	nd	0.02	0.03	0.03	0.02	nd	0.02	0.01	0.03	0.03	0.02	0.03
CaO	0.08	0.02	0.05	0.01	0.07	0.26	0.08	0.01	0.04	0.04	0.06	0.05
Na_2O	0.01	0.00	0.01	0.01	0.01	0.10	0.03	0.01	0.01	0.01	0.01	0.01
K_2O	0.02	0.00	0.01	0.02	0.01	0.14	0.03	0.01	0.01	0.01	0.02	0.01
H_2O	10.61	10.84	10.73	10.49	10.66	10.72	10.69	10.46	10.78	10.75	10.73	10.71
Total	99.14	99.20	99.22	99.00	98.84	99.25	99.11	99.03	99.04	99.30	99.02	99.02
cha %	80	67	75	81	76	80	76	83	71	72	73	74
cli %	18	32	24	18	23	19	23	16	28	27	26	25
pen %	2	1	1	1	1	1	1	1	1	1	1	1
Si	2.75	2.83	2.76	2.67	2.76	2.80	2.76	2.63	2.77	2.76	2.73	2.72
Al^{IV}	1.25	1.17	1.24	1.33	1.24	1.21	1.24	1.37	1.23	1.24	1.27	1.28
Site T	4	4	4	4	4	4	4	4	4	4	4	4
Al^{VI}	1.23	1.17	1.30	1.25	1.31	1.30	1.27	1.30	1.28	1.24	1.31	1.29
Ti	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00
Fe_{tot}	3.82	3.23	3.48	3.90	3.54	3.65	3.56	3.94	3.34	3.42	3.42	3.45
Mn	0.07	0.04	0.04	0.03	0.03	0.03	0.03	0.03	0.04	0.04	0.04	0.04
Mg	0.87	1.55	1.13	0.84	1.07	0.89	1.09	0.75	1.29	1.28	1.19	1.19
Cr	nd	0.00	0.00	0.00	0.00	nd	0.00	0.00	0.00	0.00	0.00	0.00
Ni	nd	0.00	0.00	0.00	0.00	nd	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.01	0.00	0.01	0.01	0.01	0.03	0.01	0.00	0.00	0.01	0.01	0.01
Na	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00
Site O	6.00	6.00	5.96	6.04	5.96	5.95	5.98	6.03	5.97	6.00	5.98	5.99
Fe/(Fe+Mg)	0.81	0.68	0.76	0.82	0.77	0.80	0.76	0.84	0.72	0.73	0.74	0.74
$Al^{IV}/(Si+Al^{IV})$	0.31	0.29	0.31	0.33	0.31	0.30	0.31	0.34	0.31	0.31	0.32	0.32
T [°C][1]	341	316	336	366	337	326	336	379	333	339	346	350
T [°C][2]	343	317	336	361	338	333	337	371	332	336	342	344

Explanations as in Table 1

the chlorites: chlorite grains formed within the Strzelin granite contain more MgO than the chlorite from the Borów granite (Tables 1 and 2). Therefore the lower content of magnesium in chlorites formed in the Borów granite can be related to the lower content of magnesium in the host rock. The MgO/FeO ratio in chlorite and the MgO/FeO ratio in unaltered Strzelin granite (0.32 and 0.3 respectively) and in unaltered Borów granite (0.13 and 0.08 respectively) lie very close to the 1:1 line supporting the linear dependence suggested by Cathelineau and Nieva (1985) and Shikazono and Kawahata (1987).

CHLORITE AS A GEOTHERMOMETER

Chlorite is frequently used as a geothermometer as its structure and chemical composition can reflect the physicochemical conditions of its formation. Shikazono and Kawahata (1987) found that the $Fe^{2+}/(Fe^{2+}+Mg)$ ratio differs for chlorites formed in different hydrothermal environments. Moreover, they showed that the iron content in chlorite is temperature-related. De Caritat *et al*. (1993), Cathelineau and Nieva (1985), Kranidiotis and MacLean (1987), Zang and Fyfe (1995) and other authors systematically investigated the interdependence
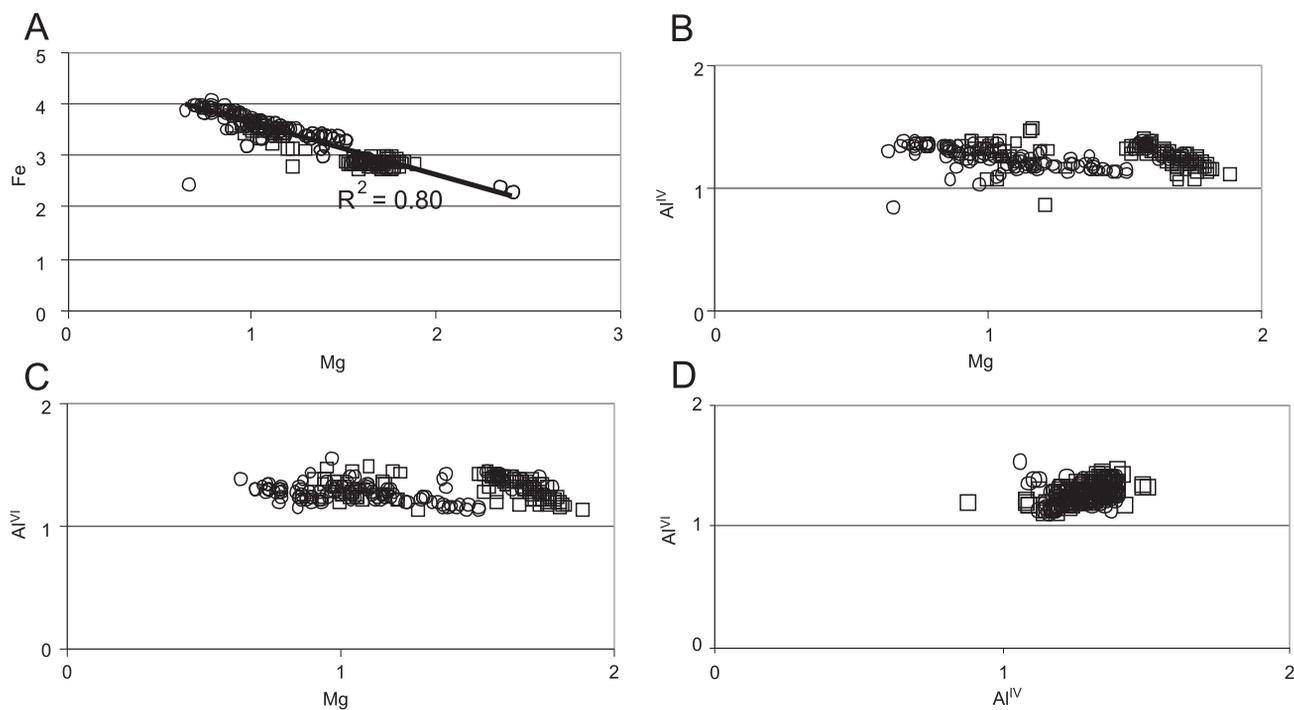
Fig. 4. Scatter diagrams of A – Fe plotted against Mg; B – Al^{IV} *versus* Mg; C – Al^{VI} *versus* Mg;
D – Al^{VI} *versus* Al^{IV} (atoms per half formula unit) in chlorite from the Strzelin (squares) and Borów (circles) granites
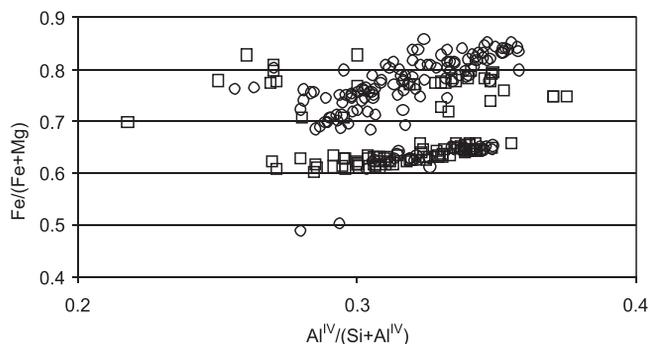

Fig. 5. Diagram of the relations of Fe^{2+}/(Fe^{2+}+Mg) *versus*
Al^{IV}/ (Si+Al^{IV})in chlorites from the Strzelin (squares)
and Borów (circles) granites

XRD data of chlorite formed in the hydrothermal veins and strongly altered zones of the Strzelin granite

Hydrothermal vein		Strongly altered granite	
d (Å)	I	d (Å)	I
14.20	40	14.15	30
7.08	100	7.06	100
4.71	40	4.72	40
3.535	60	3.536	50
2.823	30	2.828	20
2.607	20	2.610	8
2.563	5	2.568	7
2.457	10	2.458	8
2.397	7	2.399	8
2.272	10	2.270	7
2.011	10	2.015	10
		1.891	5
1.887	6	1.884	5
1.825	4	1.828	2
1.715	5		
1.658	4	1.666	2
1.566	10	1.567	8
1.540	30	1.554	5
1.515	2	1.518	2

between chlorite composition and temperature. They claim that the effects of increasing intensity of hydrothermal alteration upon chlorite composition include a decrease in Si^{IV}, Al^{VI} and structural vacancies in octahedral sites, and an increase in Al^{IV}, Fe/(Fe+Mg) ratio, and the sum of cations in octahedral sites – Σ^{VI}. Kranidiotis and MacLean (1987) calibrated the geothermometer for chlorites formed in hydrothermal environments saturated in Al, and thus in the presence of other Al-minerals. Jowett (1991, *vide* de Caritat *et al*., 1993) proposed the geothermometer (T [^{o}C] = 319Al$_c^{IV}$ – 69 with a corrected Al^{IV} value of Al$_c^{IV}$ = Al^{IV} + 0.1Fe/(Fe+Mg)), which can be used for chlorites formed in different environments, but in the temperature interval of 150–325°C with a Fe/(Fe+Mg) ratio less than 0.6. Vidal *et al.* (2001) proposed a four-thermodynamic-component solid solution model that accounts for the Tschermak, Fe-Mg, and di/trioctahedral substitutions for aluminous

(Si <3 a.p.h.f.u.) chlorite in quartz-bearing rocks. They calibrated the relevant thermodynamic data with independent sets of published experiments and natural data. A modification of the geothermometer, applicable to low-T chlorites, was proposed by Inoue *et al.* (2009). They showed that low-temperature chlorites have generally higher contents of Si and larger
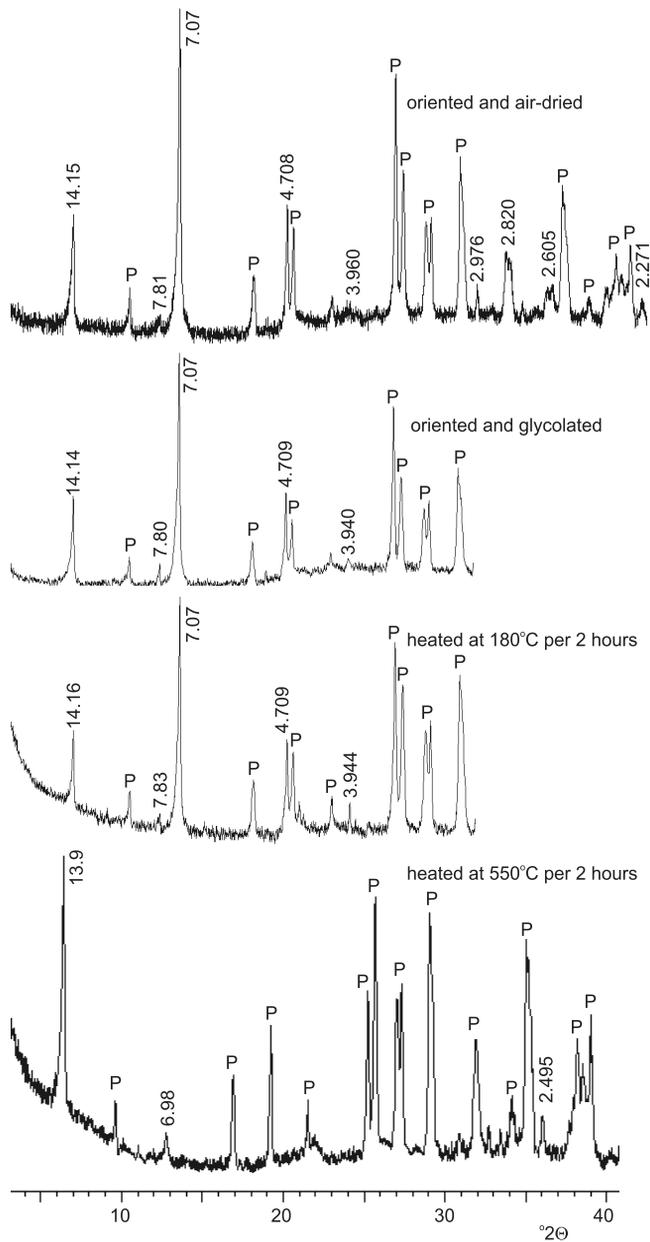
Fig. 6. XRD patterns of spherulitic chlorite formed in a hydrothermal vein in the Strzelin granite
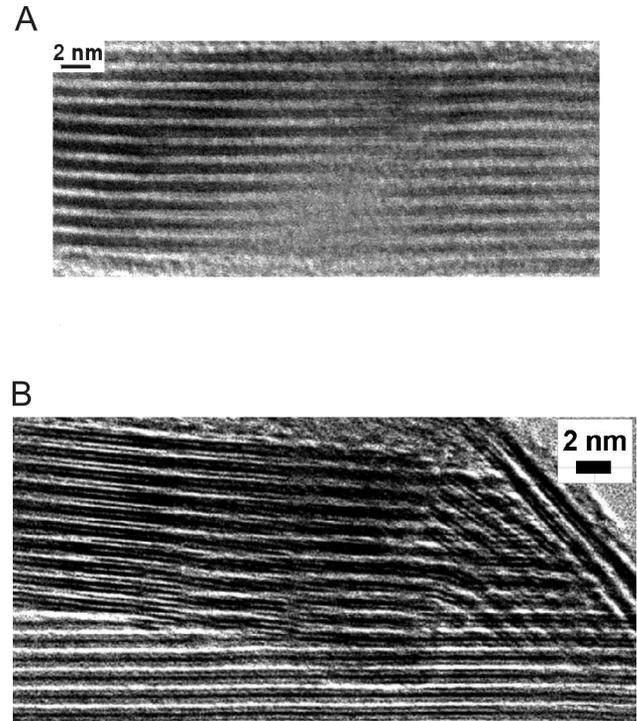
P – prehnite peaks

A

B

Fig. 7. A HRTEM image of chlorite with 14 Å periodicity

A – post-biotite chlorite formed in the unaltered Strzelin granite; **B** – post-biotite chlorite crystallised in the slightly altered Strzelin granite

$$T = 106 Al_c^{IV} + 18, \ \text{corrected } Al^{IV} \text{ value} \qquad [2]$$
$$Al_c^{IV} = Al^{IV} + 0.7 Fe/(Fe+Mg)$$
$$\text{(Kranidiotis and MacLean, 1987)}$$

Both methods reveal some interdependences between hydrothermal chlorite composition and the temperature of its formation. The inaccuracy of the Cathelieau (1988) geothermometer is ±25°C and some results are within the limit of error of the method but the tendency is the same for chlorites from both granites. The equation proposed by Kranidiotis and MacLean (1987), considering the influence of Fe and Mg amount on temperature formation, seems to be more suitable, particularly in that the chlorite formed in the Borów granite contains more Fe and less Mg than that in the Strzelin granite. According to this geothermometer the differences between calculated temperatures are smaller.

Averaged calculated temperatures of chlorite formation in the Strzelin and Borów granites is similar and varies from 326 to 371°C. In the Strzelin granite the lowest temperatures are shown by chlorite grains in unaltered granite (326°C) and the highest in the hydrothermal veins (355°C). Chlorites formed within slightly and strongly altered granite show intermediate temperatures: 341 and 342°C respectively. In the Borów granite the highest temperature are given by chlorite grains crystallised in hydrothermal veins whereas temperatures of chlorites formed within the granite are lower and reach 343°C for unaltered granite and range from 317 to 361°C with a mean of 337°C for strongly but differently altered parts of granite.

numbers of octahedral vacancies and lower contents of Fe+Mg than higher-grade metamorphic chlorites. However, it is necessary to distinguish between Fe^{2+} and Fe^{3+}, which is usually done by means of the Mössbauer spectroscopic method. The assumption that all iron is regarded as Fe^{2+} can lead to overestimation of temperature formation.

Taking into account chemical composition of chlorites formed in the Strzelin and Borów granites and restrictions of the proposed geothermometers, the following regression equations of establishing temperature T (°C) for chlorites formed under hydrothermal environments were used:

$$T = -61.92 + 321.98 Al^{IV} \text{ (Cathelineau, 1988)} \qquad [1]$$

In both granites there is a slight difference in temperature calculated for analyses made within the rims and cores of chlorite grains (in the Strzelin granite 340°C and 341°C respectively and in the Borów granite 332°C and 336°C respectively). Furthermore, clear differences observed between spherulitic and post-biotite chlorites. The temperature of spherulitic chlorite crystallization is higher (364°C in the Strzelin granite and 344°C in the Borów granite) than that for the post-biotite chlorite (340°C and 342°C respectively).

On the basis of thermometric and barometric studies of fluid inclusions in quartz Stępisiewicz (1977, 1978) estimated the temperature of chlorite formation in hydrothermal veins in the Strzelin granite generally from two hundred and tens to a hundred and tens degrees Celsius. A detailed study of the crystallisation conditions of the post-magmatic minerals formed in pegmatites and hydrothermal veins was conducted by Kozłowski and Marcinowska (2007). The temperatures and pressures of chlorite formation in the Strzelin granite were inferred from fluid inclusions present in the growth zones of quartz or fluorite or calcite where chlorite grains were included. The chlorite crystallisation temperatures lie within three intervals: 300–260°C, 210–180°C and 160–150°C. According to Janeczek (1985) the temperature of chlorite formation in the Strzegom–Sobótka Massif ranges from 400 to 230°C.

SUMMARY AND CONCLUSIONS

Chlorite is one of the most common minerals formed in granitoids at the hydrothermal stage of their formation. The assemblage of hydrothermal minerals can differ in different massifs in the world, but usually it consists of titanite, laumontite, prehnite, calcite, muscovite, clay minerals, epidote, hematite and fluorite. These minerals, as well as chlorite, are found within the granite as alteration products or as crystals formed in fractures and microfractures. The presence of interstratified structures in investigated chlorites has generally been excluded.

Chlorite grains formed in unaltered Borów granite contain more iron than these formed in the Strzelin granite. The factor which can influence on chlorite composition is the MgO/FeO ratio of the host rock, the MgO/FeO ratio of the Strzelin granite being higher than that in the Borów granite. In hydrothermally altered parts of the granites investigated chlorite of spherulitic shape is slightly more ferruginous than post-biotite chlorite, depending mostly on the chemical composition of hydrothermal fluids and oxygen fugacity, which facilitates Fe-chlorite formation. The variability of chlorite composition in the five samples of strongly altered Borów granite can be explained by multiplefluxes of hydrothermal fluid of different concentrations of components or by oxygen fugacity variation as can happen in a large active shear zone.

Increasing temperatures of chlorite formation in gradually altered Strzelin granite and lower temperature of chlorite formed within the Borów granite than in the veins show that the temperature of the hydrothermal fluid penetrating granitic bodies was higher than the temperature of the Strzelin and Borów granites at that time. Increase of the Al^{IV} contents towards the mineralisation zone may indicate increasing temperatures. Higher temperatures of spherulitic chlorite crystallisation directly from the fluid in veins indicates that this process takes less time than the process of biotite chloritisation, which starts with biotite breakdown by substitution of K^+ by H^+ followed by the alteration of tetra- and octahedral sheets. This is supported by higher formation temperatures of spherulitic chlorite by comparison with post-biotite chlorite in the Strzelin and Borów granites.

The temperature of chlorite formation in the Strzelin granite proposed by Stępisiewicz (1977) was rather underestimated. Only the upper temperature range 210°C and higher is possible, as proposed by Kozłowski and Marcinowska (2007) for the first interval. The temperature of chlorite formation in the Borów granite is in line with the estimations proposed by Janeczek (1985) and can be limited to the range 300–400°C. This means that chlorite in the Strzelin and Borów granites was formed mainly in the upper temperature range of the hydrothermal stage of granite formation. Therefore the temperature range of chlorite formation corresponds to the zeolitic-prehnite/pumpellyite facies of low-grade metamorphism. Calculated temperatures do not take into consideration the pressure, oxygen fugacity, activity of Mg^{2+} ions, sulphur concentration, pH or ionic concentration. Therefore, research still needs to be conducted to establish the dominant factor in the process of chlorite formation.

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