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Short Communication

Chlorite geothermometry and the temperature conditions at the Variscan thrust front in eastern Belgium

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Introduction

Chlorite, a mica-like clay mineral, can be found in a variety of geological environments including sedimentary, low-grade metamorphic and hydrothermally altered rocks (Deer et al. 1966). Several methods have been proposed to constrain the formation conditions of chlorite and to investigate its genesis in a given area. A chlorite solid-solution geothermometer was proposed by Cathelineau & Nieva (1985), based on a systematic investigation of the relation between chlorite composition and temperature in the Los Azufres geothermal system (Mexico). In this empirical approach, they noted that the number of tetrahedral atoms ($\mathrm{Al^{IV}}$) is strongly correlated with the precipitation temperature and that it can be described by a linear relation. The temperature can be calculated from:

$$\mathrm{T(^\circ C)} = 213.3\mathrm{Al^{IV}} + 17.5$$

Based on new chlorite analyses and microthermometric measurements of fluid inclusions in quartz crystals associated with the chlorites and on data from the Salton Sea, Cathelineau (1988) derived a new relationship between temperature and $\mathrm{Al^{IV}}$:

$$\mathrm{T(^\circ C)} = -61.92 + 321.98\mathrm{Al^{IV}}.$$

The original geothermometer of Cathelineau & Nieva (1985) should no longer be used. Jowett (1991) modified the Cathelineau expression taking into account the variation in Fe/(Fe+Mg) in chlorite:

$$\mathrm{T(^\circ C)} = 319\mathrm{Al_c^{IV}} - 69,$$

$$\text{with} \qquad \mathrm{Al_c^{IV}} = \mathrm{Al^{IV}} + 0.1[\mathrm{Fe}/(\mathrm{Fe}+\mathrm{Mg})].$$

Another approach, proposed by Walshe (1986), is based on a six-component chlorite solid-solution thermodynamic model.

In this note, quartz-chlorite-ferroan calcite shear veins in the Lower Devonian siliciclastics of the Bolland borehole have been investigated. Several of these veins are spatially related to Variscan thrust faults. The aim of this study is to apply chlorite compositional geothermometry to determine temperature conditions at the Variscan front in eastern Belgium.

Geological setting

The study has been carried out on the Lower Devonian of the Bolland borehole in the Verviers Synclinorium, eastern Belgium (Figure 1). In eastern Belgium, the basement is represented by the Brabant Massif to the north and by the Stavelot Massif to the south. Siliciclastic rocks of Early Devonian age rest unconformably on this basement. The Lower Devonian is overlain by alternating siliciclastic and carbonate series of Frasnian to Westphalian age. All these Palaeozoic rocks have been affected by the Variscan orogeny. The Verviers Synclinorium (Graulich et al. 1984) is bounded at its northern flank by the Aguesses-Asse thrust fault and at its southern flank by the Stavelot Massif (Figure 1). This Variscan tectonic unit, made up of series of Early Devonian to Namurian age, has been sliced by several other Variscan thrust faults. The Fafchamps thrust fault cross-cuts the Lower Devonian at a depth of 2133.95 m (Graulich 1984). Shear veins contain-

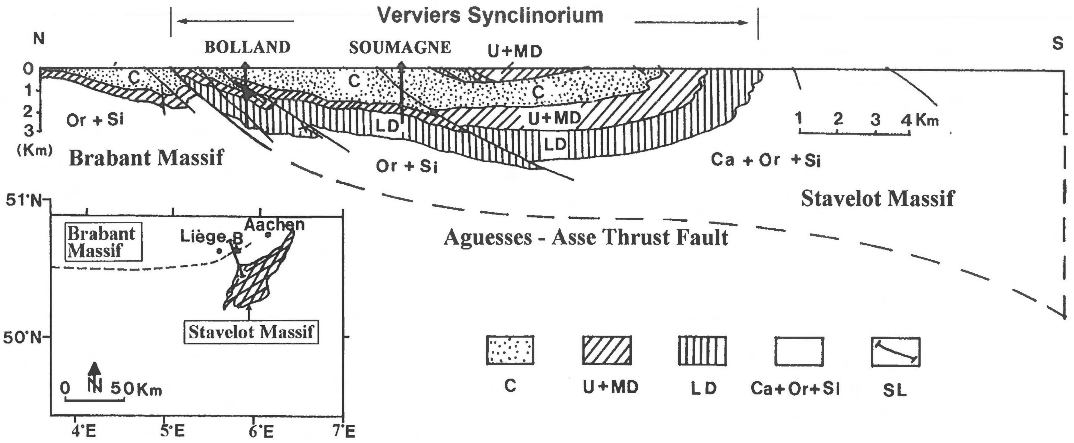

Figure 1. Cross section through the Variscan thrust front in eastern Belgium, showing the location of the Bolland borehole (simplified after Geukens, 1981 and Graulich, 1984). B: Bolland, C: Carboniferous, U+MD: Upper and Middle Devonian, LD: Lower Devonian, Ca+Or+Si: Cambrian-Ordovician-Silurian, SL: section location (inset map). Dashed line on inset map indicates southern edge of Brabant Massif.

ing quartz, chlorite and ferroan calcites are associated with this thrust fault. The Aguesses-Asse thrust fault is thought to occur just below the bottom of the Bolland borehole (Geukens 1981).

Petrography

The shear veins in the Lower Devonian of the Bolland borehole are a few centimetres to more than a decimetre wide. They have dips between 70 and 90°. Quartz, chlorite and ferroan calcites fill the shear fractures. Since several of these shear veins in the borehole are spatially related to Variscan thrust faults, they must have a Variscan age. The chlorites are colourless to green in thin section and may show a moderate pleochroism. Four different occurrences of the same chlorite group have been recognized:

- chlorite filling microfractures with a width of less than 1 μm,
- chlorite of 1–2 μm, intergrown with quartz in larger veins,
- chlorite with well-developed crystal aggregates, ranging from 1 to more than 10 μm, and intimately associated with quartz,
- chlorites discontinuously aligned along the margins of quartz veins.

The relationship between the chlorites and the quartz indicates that both minerals formed at equilibrium conditions.

Chlorite chemistry and geothermometry

Thin polished sections were prepared from the drill cores for chlorite analysis. The chlorite crystals forming crystal aggregates and intimately associated with quartz, were analysed for their silicium, aluminium, iron, manganese, magnesium and titanium contents on a Cameca France 'SX 50' electron microprobe. The size of the analysed spot was ~ 10μm. Fayalite (Si), sapphire (Al), hematite (Fe), olivine (Mg), rhodonite (Mn) and rutile (Ti) were used as standards. According to the analyses (Table 1), the chlorites have a trioctahedral structure (Hey, 1954). The largest variation in the chlorite composition is in FeO and MgO. Moreover, the sum of these oxides and therefore of the total amount of divalent cations remains constant. The number of tetrahedral aluminium atoms (calculated on the basis of 14 oxygen atoms) is 1.35–1.37 (Table 1). The Si content and Fe/(Fe+Mg) ratio have been used to classify the chlorites. The chlorites from the different levels in the Bolland borehole contain 5.13 to 5.41 Si atoms (calculated on the basis of 28 oxygen atoms) and have a Fe/(Fe+Mg) ratio of 0.45 to 0.61 (Figure 2). This is within the range of ripidolite (Hey 1954; Foster 1962).

The observation that no relation exists between the variation in the Fe/(Fe+Mg) ratio and the other chemical elements, and that the sum of the Fe and Mg contents remains constant indicates that the concentration of these elements is related to the rock composition. The Fe/(Fe+Mg) ratio in the Lower Devonian

Table 1. Microprobe analyses (in wt%) of chlorites in the Lower Devonian of the Bolland borehole (depths in metres) and calculated structural formulas based on 14 oxygen atoms.

Samples	1392 m (n = 34)	2139 m (n = 29)	2520 m (n = 28)
SiO_2	24.79	24.64	25.30
Al_2O_3	23.26	23.24	23.21
MgO	11.08	11.75	14.94
FeO*	28.16	27.75	23.50
MnO	0.20	0.20	0.16
TiO_2	0.03	0.04	0.03
H_2O	11.22	11.63	11.47
Total	98.74	99.25	98.61
Si	2.65	2.63	2.65
Al^{IV}	1.35	1.37	1.35
Al^{VI}	1.58	1.55	1.52
Fe	2.52	2.47	1.98
Mg	1.75	1.88	2.33
Mn	0.02	0.02	0.01
R^{2+}	4.30	4.36	4.40
Vac	0.12	0.09	0.08
Fe/(Fe+Mg)	0.59	0.57	0.46

* Total iron content as FeO.

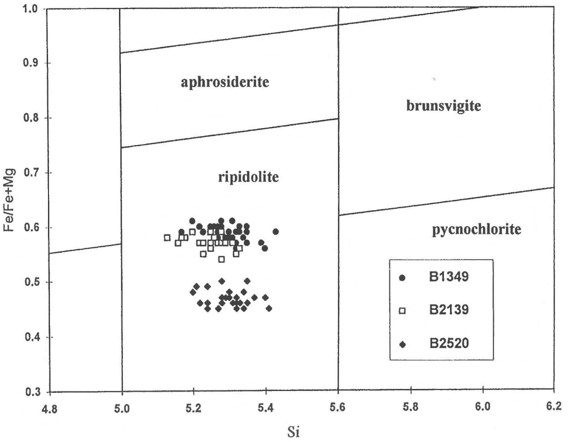

Figure 2. Plot of the Fe/(Fe+Mg) ratio versus the number of Si atoms in chlorite, Bolland borehole. Chlorite classification scheme after Hey (1954). Sample numbers refer to depths (m).

Table 2. Comparison of the precipitation temperatures of chlorites at different depths in the Bolland borehole, based on different geothermometers.

Temperature (°C)	T_1	T_2	T_3
1392 m	300.7	372.8	380.5
2139 m	312.8	379.2	386.2
2520 m	313.9	372.8	376.3

Thermometers: T_1: Walshe, 1986 (for calculation at the pressure of 1 kbar); T_2: Cathelineau, 1988; T_3: Jowett, 1991.

schists around the Stavelot Massif is between 0.32 and 0.60 (Fieremans, 1982), but can be as much as 0.78 (Kramm, 1982). This range is similar to that observed in the chlorites analysed. This further suggests that the number of tetrahedral aluminium atoms is related to precipitation temperature and can be used for geothermometry. The calculated temperature for chlorite precipitation (Table 2) using the model of Walshe (1986) is about 310 °C. The equations of Cathelineau (1988) and Jowett (1991) give temperatures of ~ 380 °C.

Discussion

The maximum burial temperature of the Lower Devonian in the Verviers Synclinorium is between 245 and 310 °C (Helsen 1995). The calculated temperature of 310 °C using the model of Walshe (1986) is at the upper limit of this range. The equations of Cathelineau (1988) and Jowett (1991) give temperatures which are ~ 70 °C higher. A temperature of 380 °C would imply either a much deeper origin for the fluids or their lateral migration from the metamorphic zone of the Stavelot Massif. In the metamorphic zone in the southern part of the Stavelot Massif, temperatures between 360 and 420 °C have been determined (Kramm 1982; Fransolet & Kramm 1983). Although such an origin of the fluids is possible, several points of evidence suggest a lower temperature of the ambient fluid at the site of chlorite precipitation.

Aqueous fluid inclusions in quartz crystals associated with the chlorite crystals have a maximum homogenization temperature of 188 °C (Zhang, unpublished data). Taking into account a pressure correction of 130 MPa (5 km lithostatic pressure), a maximum trapping temperature of 264 °C can be calculated (Brown 1989).

In the Jowett (1991) geothermometer, a relation between the Fe/(Fe+Mg) ratio and the precipitation temperature of the chlorites is implied. In our study, the Fe/(Fe+Mg) ratio is independent of the number of tetrahedral aluminium atoms. The empirical methods are not based on any thermodynamic foundation and are therefore not expected, in principle, to yield similar results to a thermodynamic approach (De Caritat et al. 1993). No geothermometer performs satisfactorily over the whole range of natural conditions (different temperatures, coexisting assemblages, Fe/(Fe+Mg), fO_2, etc.). More recent versions of any chlorite geothermometer are not necessarily better than the previous ones, particularly when they are based on different concepts. The empirical calibration methods are certainly applicable in the area where they have been defined, but cannot be generalized to other rock types and areas.

Numerical modelling of the palaeotemperature field at the Variscan thrust front in western Germany indicates that the maximum temperature along the thrust faults, considering conductive and convective heat transport, is 310 °C (B. Lünenschloss, unpublished data). Our results agree with an earlier study by Hein (1993), who suggested that the temperatures obtained from Variscan chlorites using the equations of Cathelineau (1988) and Jowett (1991) are 50 to 70 °C too high.

A characteristic feature of the calculated chlorite precipitation temperatures is that the same temperature has been found in the Bolland borehole at depths differing by more than 1 km (Table 2), independent of the geothermometer used. This indicates that this uniform temperature distribution is real. It can be explained by a rapid upward fluid flow along the faults, modifying the temperature field.

Conclusion

The calculated temperature conditions of the chlorite formation in the shear veins and therefore also of the Variscan thrusting depend on the geothermometer used. The thermodynamic model of Walshe (1986) gives a temperature around 310 °C, which is similar to the temperature conditions during maximum burial of the Lower Devonian sediments. The empirical models of Cathelineau (1988) and Jowett (1991) indicate ~ 380 °C. Although such a temperature cannot be excluded, there are several points in favour of the first model.

The chlorite precipitation temperature is uniform in the Lower Devonian of the Bolland borehole, suggesting rapid upward fluid flow along the faults.

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