Annales Societatis Geologorum Poloniae (2009), vol. 79: 147–158.

ISOTOPIC MASS BALANCE OF METAMORPHIC FLUIDS IN THE GOGOŁÓW–JORDANÓW SERPENTINITE MASSIF, LOWER SILESIA, SW POLAND

Adam MYDŁOWSKI

Polish Geological Institute, Lower Silesian Branch, Jaworowa 19, 53-122 Wrocław, Poland; e-mail: adam.mydlowski@pgi.gov.pl

Mydłowski, A., 2009. Isotopic mass balance of metamorphic fluids in the Gogołów–Jordanów serpentinite massif, Lower Silesia, SW Poland. *Annales Societatis Geologorum Poloniae*, 79: 147–158.

Abstract: This work aims at estimation of the amount of metamorphic fluids which led to the present-day variability of isotopic compositions, δD and $\delta^{18}O$, in serpentinites from the Gogołów–Jordanów Massif. This goal was achieved by means of a numerical model reproducing selected features of geological environment and a computer application supporting this model. The Gogołów–Jordanów Massif consists of peridotites transformed to a different degree into serpentinites and subject to brittle deformation that produced a complex fracture system. The potential tectonic control on the pattern of the fluid migration paths was investigated using palaeostress analysis based on slickenside measurements. Isotopic analyses were carried out for hydrogen and oxygen from serpentine, oxygen from magnetite, and hydrogen and oxygen from carbonates. The variability of δD and $\delta^{18}O$ in the serpentinites along the modelled migration paths demonstrates that serpentinization of peridotites was caused by fluids derived from at least three sources revealing different isotopic characteristics. Fluids produced during the magmatic-hydrothermal stage played a major role in serpetinization, since they represent approximately 95% of all fluids interacting with the rock. In contrast, oceanic water represents only 1% of fluids involved in serpentinization. The calculated mean amount of fluid required for serpentinization of 1 m^3 of peridotite is equal to $98 \cdot 10^4$ kg.

Key words: serpentinization, stable isotope, tectonics, numerical modelling, Gogołów–Joradanów Massif, Lower Silesia, SW Poland.

Manuscript received 30 September 2008, accepted 27 July 2009

INTRODUCTION

For the last thirty years the vast amount of work has been done to document the origin, evolution and tectonic position of the Ślęża ophiolite complex (Majerowicz, 2006 and references therein). Consequently, there is no doubt today that the Ślęża complex represents a fossil remnant of ocean floor obducted on continental crust during the Variscan orogeny. Nevertheless, some open questions remain concerning the timing and mechanism of serpentinization that affected the ultramafic member of the Ślęża ophiolite. Uncertain is the source of serpentinizing fluids and the paths of their infiltration into the ultrabasic rocks. Some of these questions are addressed in the present paper that is focused on the mass balance of metamorphic fluids accompanying metamorphism of primary ultramafic rocks of the Gogołów–Jordanów serpentinite massif. Considerable progress in digital processing of data allows calculation of the mass of fluids (Taylor, 1977; Vollmer, 1976; Sverjensky, 1981; Zheng & Hoefs, 1993) using a channelized flow model (Fyfe *et al.*, 1978; Thompson, 1987). A key role of the canalised fluid transfer in large-scale metamorphic processes, especially during serpentinization of ultramafic rocks and dehydratation of serpentinites, is emphasized in the majority of up-to-date papers dealing with these issues (*e.g.*, Oliver, 1996; Ord & Oliver, 1997; Barnes *et al.*, 2004; Masters & Ague, 2005). Therefore, the model of fluid migration paths presented herein does not take into account the possibility of penetrative infiltration of fluids throughout the ultramafic rocks due to massive development of microcracks. The growth of such discrete fractures may be a consequence of volume-changing chemical reactions, connected for instance with hydratation, resulting in local perturbations of the stress field (*e.g.*, Watt *et al.*, 2000; Malthe-Sørenssen *et al.*, 2006). The common development of discrete fractures may produce local permeability changes that promote fluid flow. The modelling of fluid migration assisted by penetrative fracturing would require an application of the finite element method. However, this approach cannot be implemented to the presented numerical model.

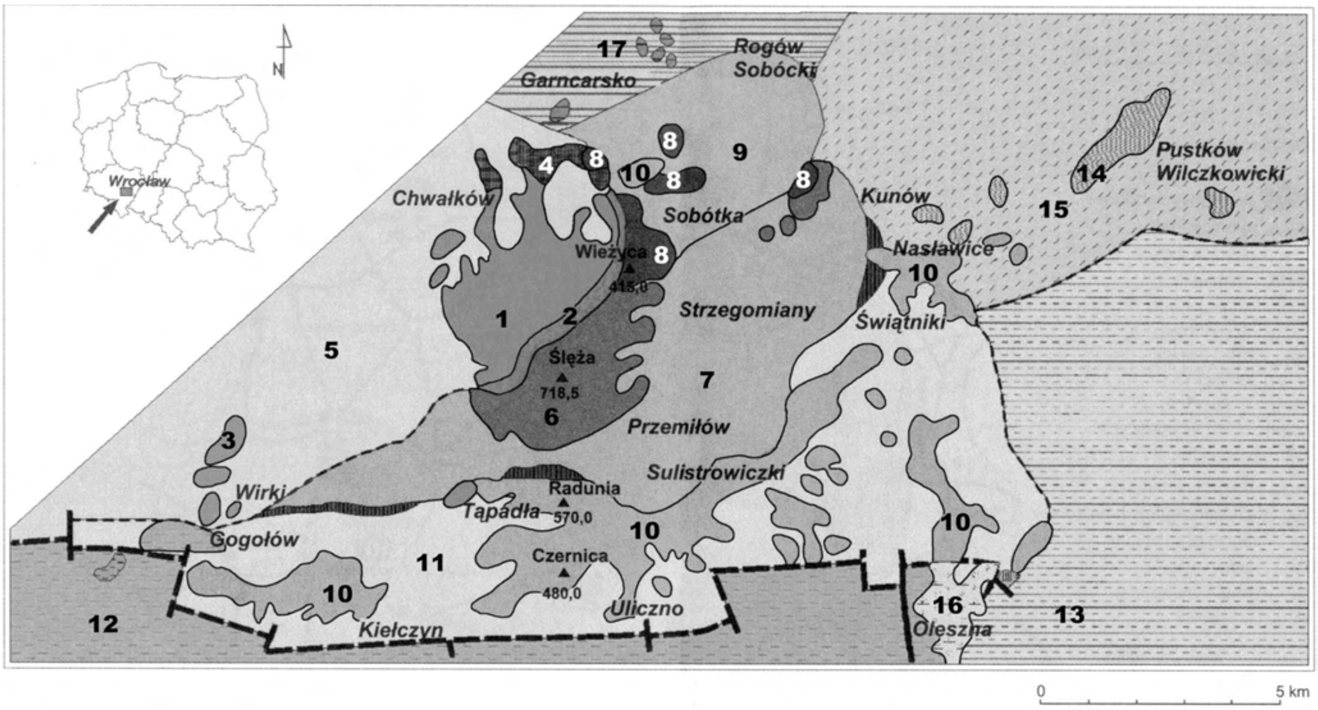


Fig. 1. Geological sketch map of the Ślęża environs (based on Majerowicz, 1995, 2006): 1 – biotite granodiorite, 2 – granite around the contact zone of amphibolites, gabbro, and serpentinites, 3 – Wierzbice two-mica granite, 4 – alaskite metagranite, 5 – undivided granitoids, covered, 6 – metagabbro, 7 – metagabbro, covered, 8 – amphibolites, 9 – amphibolites, covered, 10 – serpentinites of the Gogołów–Jordanów massif, 11 – serpentinites, covered, 12 – gneisses of the Góry Sowie Mts., 13 – gneisses of the eastern cover of the Ślęża Massif, 14 – phyllites, epimetamorphic greywacke and silliceous schists, 15 – phyllites, epimetamorphic greywacke and silliceous schists, covered, 16 – mylonites, 17 – metamorphic schists

Furthermore, any examples of fluid transport models successfully integrating canalised flow and penetrative migration are hitherto missing from scientific literature. The significance of the latter process has not been so far reliably estimated elsewhere and, thus, has been omitted here.

The modelling of the potential fluid paths was supported by a palaeostress analysis based on slickenside data, which were processed using Tectonics FP software. A simplified model of the Gogołów–Jordanów serpentinite massif was created to reconstruct the migration of fluids responsible for serpentinization. The model was implemented using a produced in-house computer application. The isotope data employed in the model were derived from laboratory analysis of oriented serpentinite samples. Isotopic analyses of hydrogen and oxygen from serpentinite, oxygen from magnetite, and carbon and oxygen from carbonates were obtained for 173 samples.

GEOLOGICAL SETTING

Ślęża Ophiolite Complex

Mafic and ultramafic rocks in the vicinity of the Ślęża Mt. form a nearly complete ophiolite association including serpentinized peridotites, a narrow zone of metamorphosed ultramafic cumulates, metagabbros and metabasalt volcanic suite accompanied by a sheeted dyke complex (Majerowicz, 1979, 1981, 1984; Majerowicz & Pin, 1989, 1994; Pin *et al.*, 1988). The Ślęża ophiolite is in tectonic contact with the low-grade metamorphosed phyllites, cherts and radiolarites that adjoin the ophiolite complex from the north. In the south, the Ślęża ophiolite borders on the Góry Sowie gneiss massif being separated from one another by a Neogene E–W trending fault system. According to Majerowicz and Pin (1989), the geochemical data suggest (1) the co-magmatic origin for all the ophiolite segments, (2) the occurrence of mafic cumulates, and (3) the resemblance to magmas generated in a MOR or back-arc setting. The estimates of δD and $\delta^{18}O$ point to sea-floor metamorphism of the ophiolite (Jędrysek & Hałas, 1989). During obduction of the ophiolite the metagabbros recorded the younger metamorphic overprint under greenschist facies conditions (Majerowicz *et al.*, 2000; Floyd *et al.*, 2002). Floyd *et al.* (2002) suggest, in contrast to the earlier studies (*e.g.*, Majerowicz & Pin, 1989, 1994), that the differences between volcanic and plutonic members of the Ślęża ophiolite preclude their affiliation to one coherent ophiolitic suite.

The Ślęża ophiolite has been originally interpreted as individual intrusions of mafic and ultramafic magmas in their present-day setting (Finckh, 1928; Teisseyre *et al.*, 1960; Oberc, 1972). Since the beginning of the 1980s, a consensus has been achieved that the Ślęża ophiolite represents a vestige of oceanic crust (Majerowicz, 1979, 1981; Narębski *et al.*, 1982; Majerowicz & Pin, 1986). Consequently, the tectonic models postulating the allochthonous position of the ophiolite began to predominate (Znosko, 1981; Quenardel *et al.*, 1988; Cymerman, 1987). The majority of recent tectonic interpretations are based on pseudo-stratigraphy of the ophiolitic complex with a younging direction towards the north. Basing on the results of his structural analysis, including joints and slickensides, Jędrysek (1985) suggested that the entire ophiolite is in an overturned position with the sepentinites occupying a structurally highest level. According to Majerowicz and Pin (1989, 1994), the ophiolite is thrust over towards the north on the low-grade metamorphic phyllitic basement. Mierzejewski and Abdel-Wahed (2000) postulate two phases of deformation, both being associated with displacements along the low-angle dislocations dipping to the east. In the tectonic model recently presented by Winchester *et al.* (2002) for the northern part of the Bohemian Massif, the Ślęża ophiolite represents the uppermost unit in a nappe pile overthrust towards the west during the Variscan orogeny. The time of early serpentinization in ultramafic rocks of the Ślęża ophiolite has been dated at 400±3 Ma basing on the zircon ages, which were obtained for the rodingite from Nasławice (Dubińska *et al.*, 2004). This age is consistent with the earlier dating of the Ślęża gabbro, the protolith of which was dated at *ca*. 420 Ma (Oliver *et al.*, 1993). The whole rock Sm-Nd age of 353±21 Ma, obtained for the Ślęża ophiolite by Pin *et al.* (1988), presumably corresponds to metamorphism or cooling of the ophiolite complex.

The Gogołów–Jordanów Massif consists of serpeninized ultramafic rocks that crop out in the area of 90 km^2. The massif belongs to a group of mafic-ultramafic ophiolite members that surround the Sowie Góry gneissic massif. It includes peridotitic rocks, which underwent serpentinization to a different degree. To the south, the serpentinites are in tectonic contact with the Sowie Góry gneisses via a system of Neogene faults. To the north, they contact with ultramafic cumulates and gabbros, and to the NW with granitoids of the Strzegom–Sobótka Massif. This boundary is covered by Cenozoic strata, like that of the Gogołów–Jordanów Massif with Palaeozoic metamorphic series (phyllites) on the east.

Brightly-coloroured, fine-grained vein rocks present in serpentinites include aplites and associated granitoids. Some of these rocks, like those exposed at Czarna Góra Mt. (Spangenberg, 1943) or in a magnesite mine at Wiry (Sachanbiński, 1984), represent plagiogranites. Chromite deposits occur as lenses at Czarna Góra and near the Tąpadła Pass, close to the boundary with ultramafic cumulates (Spangenberg, 1943; Birecki, 1962). Formation of the chromite bodies was probably associated with mantle magmatism in a regime of transfom faults (Gunia, 1989).

METHODS

Field and laboratory work

The principal aim of the field work was mesostructural analysis and collection of samples for chemical, X-ray, and isotopic analyses. Both chemical and isotopic analyses were aimed at estimating mutual relationships between isotopic composition of hydrogen and oxygen and the orientation of brittle structures. Oriented rock samples were collected manually from previously measured joint surfaces and slickensided surfaces. Samples for isotopic analyses were treated mechanically to obtain powdered material.

Vacuum isotopic preparation is used to obtain selected elements derived from the rock in a gaseous state. The common feature of these procedures is cryogenic cleaning of the gases that enables measuring isotopic composition of the latter in a mass spectrometer. For isotopic analysis it is necessary to obtain hydrogen and oxygen from silicates, and carbon dioxide from carbonates.

Analyses of isotopic composition of oxygen and hydrogen were made in the Department of Isotopic Geology and Geoecology of the Institute of Geological Sciences, University of Wroclaw, in the Laboratory for Mass Spectrometry of the Faculty of Physics and Applied Informatics of the AGH University of Science and Technology, as well as in the Department of Geological Sciences, Indiana University, Bloomington, USA. The Finnigan Mat delta E, Finnigan MAT 252, and Varian Mat CH7 spectrometers were used. Determinations of the carbonate contents and isotopic analyses of carbon and oxygen derived from carbonates were conducted in the Department of Isotopic Geology and Geoecology, Institute of Geological Sciences, University of Wrocław, using the Finnigan Mat delta E mass spectrometer.

Numerical modelling

The principal aim of this work was to construct and implement a digital model portraying the intensity of metamorphic fluid migration, with the use of isotopic mass balance. The model is mainly aimed at estimating the scale and directions of migration of serpentinizing fluids, as well as at explaining the interaction of these fluids with ultramafic rocks using the process of Rayleigh distillation. The model is based on a basic assumption of channelized fluid migration in the rock. The presented model is a static homomorphic model. The input data were discretised and subdivided into calculation blocks of identical spatial dimensions.

The main source of input data are pieces of information comprised in the data base, such as orientation of joints, slickensides and tectonic straie, as well as isotopic analyses of oriented samples.

Taking into account complicated geological structure and the lack of possibililties of determining principal tectonic directions in the field, a method of clustering planar structures was used (Mydłowski & Jędrysek, 2004). Orientation of a given fracture set was determined basing on the angle comprised between the selected pairs of readings, *i.e.* the angle between vectors perpendicular to the fractures plotted on the Schmidt's net. The angle was calculated in the following way:

For each pair of angles: azimuth of the dip a_i and dip β_i, the coefficients x_i, y_i, z_i were determined:

$$\begin{aligned} x_i &\quad \cos\ _i \sin\ _i \\ y_i &\quad \sin\ _i \sin\ _i \\ z_i &\quad \cos\ _i \end{aligned} \tag{1}$$

The angle between the selected pairs of measurements is (Mydłowski & Jędrysek, 2004):

$$\arccos \frac{x_1\ x_2 \quad y_1\ y_2 \quad z_1\ z_2}{\sqrt{x_1^2 \quad y_1^2\ z_1^2}\ \sqrt{x_2^2 \quad y_2^2 \quad z_2^2}} \tag{2}$$

Determination of the average value of angle γ between the selected measuring point and the remaining points provides a basis for distinguishing individual groups of measurements, their number and spatial orientation.

In order to visualise the input structural data and the effects of their clustering, a tool was devised to project selected structures on the Schmidt's net, enabling the immediate overview of readings collected from a given exposure.

Computational procedures used for each of the exposures made it possible to collect a set of data which embraces both orientation of the structures and the results of isotopic and chemical analyses. The data obtained provided a basis for defining sets of potential paths of metamorphic fluids. The presence of such paths is based on an assumption that fluids migrated through the rock massif utilising fractures, which, in gross part have been continuous and open for fluid migration (Jędrysek, 1989; Jędrysek & Hałas, 1989). Such fractures could have represented potential paths of serpentinizing fluids, and their spatial distribution was analysed qualitatively. To determine privileged orientations of tectonic principal stresses in the Gogołów–Jordanów Massif, techniques of palaeostress analysis were used. These orientations were associated with the tectonic regime that existed during serpentinization of the rocks, and became a reference point for the results of modelling of fluid migration paths based on isotopic composition of minerals. Visualisation of the respective stress field was made for the NDA (Spang, 1972), inversion (Angelier & Goguel, 1979; Angelier, 1979), and right dihedra methods (Angelier & Mechler, 1977). To obtain the expected stress pattern at every point of the study area, the axes of maximum compression calculated for every exposure were interpolated for the entire study area. The same procedure was applied in relation to the minimum and neutral stress axes.

For the sake of the model, a temperature calculator was constructed basing on curves of a isotopic fractionation, enabling fast conversion of the coefficient of a isotopic fractionation into the Δ value and vice versa. It is also possible to read temperatures at a given value of a, *i.e.* the coefficient of isotopic fractionation basing on a selected curve for a known temperature. Interactive plot of α vs. t°C portrays the trend of selected curves of isotopic fractionation in the required temperature range. Moreover, a possibility exists to select the required curve from the library of isotopic fractionation curves obtained from the SIFC (*Stable Isotope Fractionation Calculator*; Beaudoin & Therrien, 2004) and from other sources, what enhances the model flexibility and makes the choice of a given curve much more reliable (*e.g.*, Wenner & Taylor, 1973; Sakai & Tsutsumi, 1978; Graham *et al.*, 1980, 1987; Satake & Matsuo, 1984; Saccocia *et al.*, 2001) at a stage of model construction. The temperature calculator is active in other tasks of the model, being then activated without the graphic part providing only the results of calculations.

Application of the Rayleigh distillation model made it possible to determine the extent and variability of δD and δ^{18}O of the rock and fluid in respect to the temperature and advancement (F) of the reaction (Rayleigh, 1896; Hoefs, 1996; Valley & Cole, 2001). In order to determine the molar proportions of water/rock interactions, the geochemical and structural parts of the model were used. Both the initial isotopic composition, as well as the temperature and water-to-rock molar ratio of the solution entering the massif represent unkown values. The base of determination of the water-to-rock ratio is the set of values of δD and δ^{18}O of the rock, arranged according to a given fluid migration path, *i.e.* in the order of the progressing reaction. There is a link between each pair of the δD – δ^{18}O values of the rock and a given point on the surface of the study area. Using an iterrative technique, the shape of curvature of the model variability of δD – δ^{18}O was applied to the real course of δD – δ^{18}O from a given migration path through the relevant change of temperature of reaction, the initial isotopic composition of the solution, and the water-to-rock ratio. The result is given together with the degree of fitness (Łomnicki, 1999) to the set of real values of δD and δ^{18}O, showing that fragment of the migration path which meets the assumed criteria of the goodness of fit. Visualisation marks the selected fragment of the fluid migration path in a 3D view of the study area.

The proposed model makes it possible to trace relationships between individual areas of the studied serpentinite massif, the temperature of serpentinization, and mutual share of the given water types in shaping the recent isotopic composition of hydrogen and oxygen of the serpentinites. For each path occupying the known surface of the study area, it is possible to calculate the rock mass, which, together with the known water-to-rock molar ratio makes it possible to determine the minimal mass of serpentiniziting fluid entering the massif. Moreover, knowing the remaining fraction of fluid, F, at each point of the study area, it is possible to calculate the intensity of serpentinization and probable sites of fluid vanishing.

An application was constructed which enabled proper activity of the model calculating the isotopic mass balance of serpentinizing fluids. When constructing this application, the extreme programming was used (eXtreme Programming, XP), except the pair programming. The program in uncompiled version includes 16,120 code lines.

RESULTS AND DISCUSSION

In this paper, I used 511 measurements of fractures and slickensides, as well as 102 oriented samples collected from 37 exposures. Together with additional analyses, 76 isotopic analyses of hydrogen from the group OH, 52 oxygen analyses of silicates, 11 oxygen analyses from magnetite, and 34 isotopic analyses of carbon and oxygen from carbonates were made.

The results of hydrogen isotopic analyses (δD) of serpentinite rocks vary from –102.3 ‰ to –13.4 ‰, whereas those of the Ślęża gabbros bordering from the north the Gogołów–Jordanów Massif range between –49.6 ‰ and –2.9 ‰. The highest values of δ^{18}O of serpentine attains 11.15 ‰, the lowest is 1.45 ‰. For the gabbros, the δ^{18}O values are 7.32 ‰ and 5.48 ‰, respectively. From some samples, it was possible to obtain magnetite, the d oxygen values of which ranged between 0.44 ‰ and 5.85 ‰. Differences of hydrogen Δ ($\delta_{max} - \delta_{min}$) from serpentine between samples oriented in the scale of individual exposures, are remarkable (Fig. 2).

The water-to-rock molar ratio in relation to the Rayleigh distillation

Before incorporating hydrogen particles from the fluid into ultramafic rock during serpentinization, the water-to-rock molar ratio (W/R) should be close to infinity for the hydrogen, and after the reaction is finished it should approach zero (all hydrogen reacted with the rock). However, the hitherto used formula for the W/R ratio (Taylor, 1977), directly applied to the Rayleigh distillation model, implies that this ratio will never attain the entire range of values (∞:0).

Attempts at determining the W/R ratio, using the rule published by Taylor (1977) in relation to the Rayleigh distillation, were unsuccessful. According to the author, the W/R ratio at the onset of reaction of serpentinizing fluids is approximated best by the following formula (Mydłowski, 2006):

$$\frac{W}{R} \quad \frac{(\ {}^{f}_{rrz} \quad {}^{i}_{rrz})}{(\ {}^{i}_{w} \quad {}^{f}_{rrz})} \tag{3}$$

where:

– $\delta_{rrz}{}^{i}$, $\delta_{rrz}{}^{f}$ are the initial and final, respectively, genuine isotopic composition of the rock measured in a sample,

– $\delta_{w}{}^{i}$ is the initial isotopic composition of the fluid = the final expected composition of the rock (the final isotopic rock composition resulting from the Rayleigh distillation model).

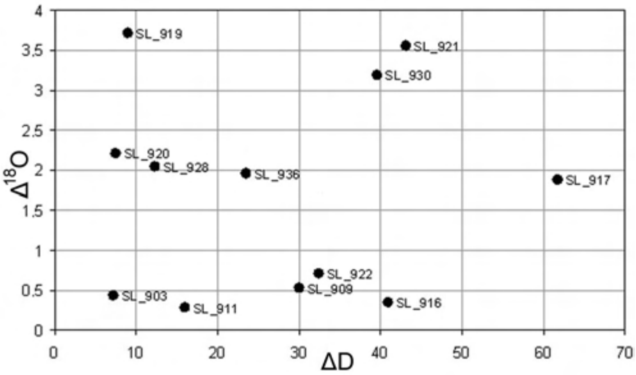


Fig. 2. Comparison of Δ ($\delta_{max} - \delta_{min}$) hydrogen and oxygen values in the serpentine between oriented samples at the single outcrop scale

The water-to-rock molar ratio will attain values derived from a set of real positive values. Knowing W/R values before the isotope exchange reaction starts is of crucial importance in estimating the amount of fluid reacting with the rock and its further influence on metamorphosis.

A summary characterizing potential possibilities of channelized fluid migration (Fyfe *et al.*, 1978; Thompson, 1987) in the Gogołów–Jordanów Massif (Jędrysek, 1989; Jędrysek & Hałas, 1989) is shown in Fig. 3.

A number of scenarios including different origin, their amounts and temperatures of reaction with the rock, which could have led to the present values of δD and $\delta^{18}O$ may be generated. Therefore, it was assumed that if recent isotopic composition of serpentinites of the Gogołów–Jordanów Massif can be achieved at the lowest possible number of fluids and at the greatest possible amounts of the latter. Hence, the modelling started with the most simple scenario, including one-stage serpentinization.

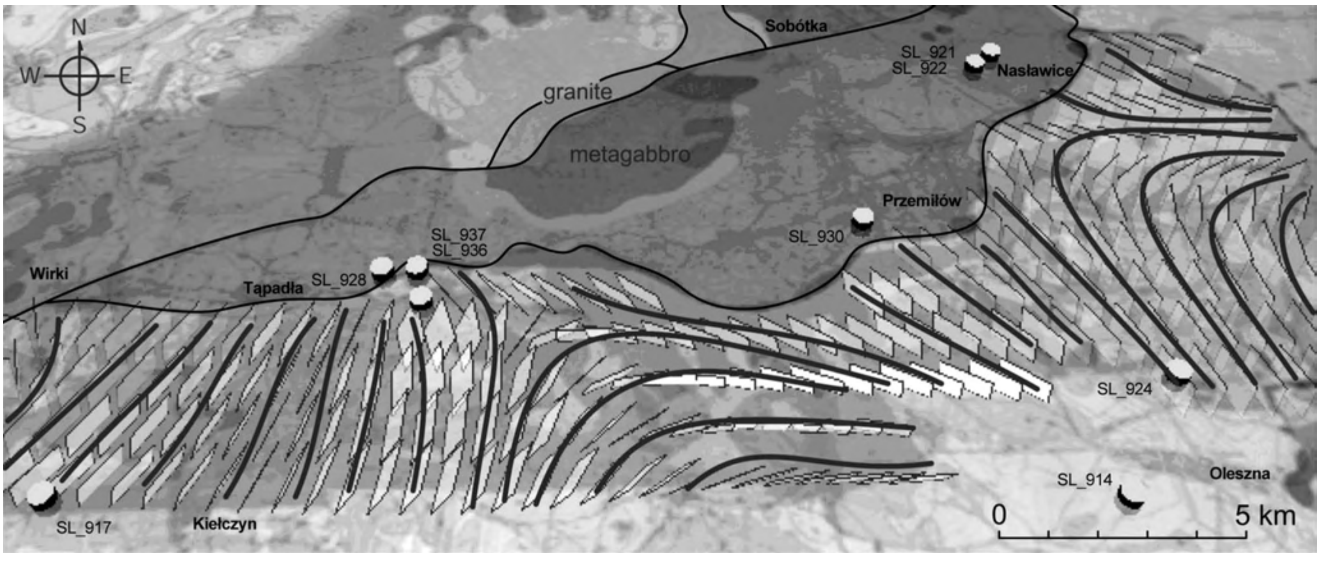


Fig. 3. 3D view of the migration path of serpentinized fluids from selected path's group on the background of geological map. The squares explain the local orientation of joint surfaces. The black curves shows predictable direction of the migration paths through the Gogołów-Jordanów Massif. The selected outcrops are also marked

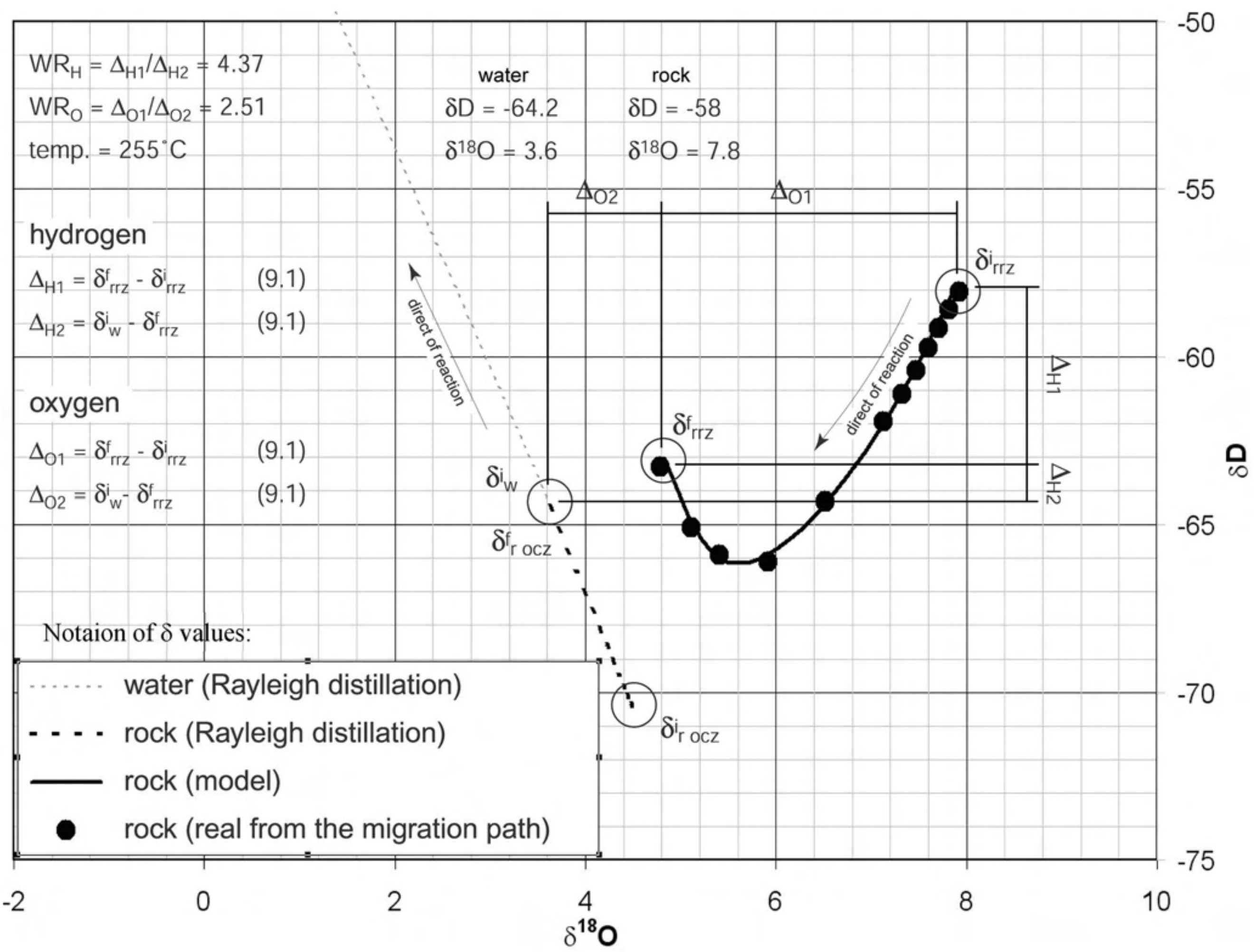


Fig. 4. Graphic interpretation of water-to-rock molar ratio in the δD – δ^{18}O space with marked initial isotopic composition of the rock, variability δD and δ^{18}O of rock from selected migration path, and adjusted to model δD and δ^{18}O of the rock. Explanations: δ^{i}_{rrz}, δ^{f}_{rrz} – initial and final real isotopic composition of rock, respectively – isotopic composition from the rock-sample measured; δ^{i}_{w} – initial isotopic composition of fluid = final expected isotopic composition of rock (final isotopic composition of rock according to Rayleigh distillation); $\delta^{i}_{r\ ocz}$ – initial expected isotopic composition of rock; $\delta^{f}_{r\ ocz}$ – final expected isotopic composition of the rock

One-stage serpentinization

The aim of one-stage modelling of serpentinization of the Gogołów–Jordanów Massif is to explain isotopic variability of hydrogen and oxygen in the most simple, possible way. Should this model be true, it would contradict the results obtained by other authors, who applied different methods (Jędrysek & Sachanbiński, 1994). One stage of serpentinization means that the recent isotopic composition of the rock (δD and δ^{18}O) originated in each migration path due to reaction with a defined amount of fluid, genetically associated with one source and of known temperature of reaction (Fig. 4).

Two-stage serpentinization

A two-stage model of serpentinization should enable the reaction of rock masses with two fluids of any isotopic composition (δD, δ^{18}O), temperature, and the amount of ($W/R_{(H,O)}$). The fluid entering the massif in the second stage reacts with the rock of isotopic composition modified by a fluid of the first stage. The two-stage modelling should be preceded by verification whether the presence of two fluids is sufficient to change isotopic composition of ultramafic rock (δD, δ^{18}O) to the present-day state (reverse modelling), keeping the δD and δ^{18}O values of delivery sources known from natural environment. This can be verified by using graphic construction shown in Fig. 5.

Multi-stage serpentinization

A model of multi-stage serpentinization should enable one to examine the vulnerability of isotopic composition of the rock (δD, δ^{18}O) to changes resulting from δD and δ^{18}O of water, temperature of reaction, and molar ratios $W/R_{(H,O)}$ for several consecutive stages. It is associated with the influence, on the same rock mass, of several, consecutive serpentinizing fluids of variable isotopic composition (δD, δ^{18}O), different temperature, and the amount of ($W/R_{(H,O)}$). Fluid of the following, younger stage modifies isotopic

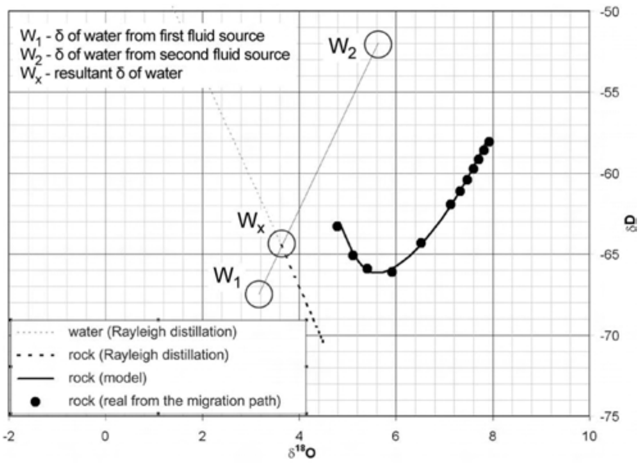


Fig. 5. Arrangement of two fluid sources with respect to hypothetic fluid source determined in one-stage serpentinization model

composition of the rock, already altered by fluids active during previous stages of serpentinization. In this sense, the molar ratio $W/R_{(H,O)}$ acquires a new meaning, constraining molar proportions of water from a given stage of serpentinization in respect to the rock altered by previous fluids.

The basic task preceding multi-stage modelling consists in verifying whether the presence of at least three fluids is sufficient for changing isotopic composition (δD, $\delta^{18}O$) of ultramafic rock to the present-day state (reverse modelling), maintaining at the same time the δD and $\delta^{18}O$ values of delivery sources found in natural environment. Fig. 6 shows graphic interpretation of such a verification.

Each of three isotopic delivery sources A, B, C can be located at a point (δD, $\delta^{18}O$), whose deviation (ΔD, $\Delta^{18}O$) from the isotopic composition of the rock is inversely proportional to the W/R molar ratio (W/R_A, W/R_B, W/R_C). The $\Delta D/\Delta^{18}O$ ratio is dependent on molar proportions between hydrogen and oxygen within the fluid and the rock. In case of pure distilled water, this proportion equals to 2. This figure may insignificantly shift depending on the solution's pH: rising at low pH, and falling at high pH. The hydrogen/oxygen molar ratio for peridotite approaches zero, while for serpentine it is close to 2/7 (Taylor, 1974). Moreover, each of three isotopic delivery sources A, B, C is limited by environmental constraints. The pattern presented in Fig. 6 implies that contemporary isotopic composition ($\delta^{18}O$ and δD) of serpentinite, as a combined product of isotopic delivery sources, could have originated due to the influence of three sources: oceanic, magmatic, and meteoric. It was accepted that $\delta^{18}O$ and δD values of meteoric water (source C) match those of the Wrocław water (Duliński *et al.*, 2001). Water of magmatic origin has the greatest share in modelling variability of $\delta^{18}O$ and δD in serpentinite, owing to high W/R_B ratio, while waters of oceanic and meteoric origin are of minor importance. Assuming that source B is compatible with isotopic composition of metamorphic or formation waters of lower δD and higher $\delta^{18}O$ ranges, the W/R ratio of source B would be lower, and fractions of A and C sources should increase, to obtain the same joint product of $\delta^{18}O$ and δD, typical for serpentinite. The model shown in Fig. 6 is a general one, and does not take into account all factors controlling the real isotopic composition of

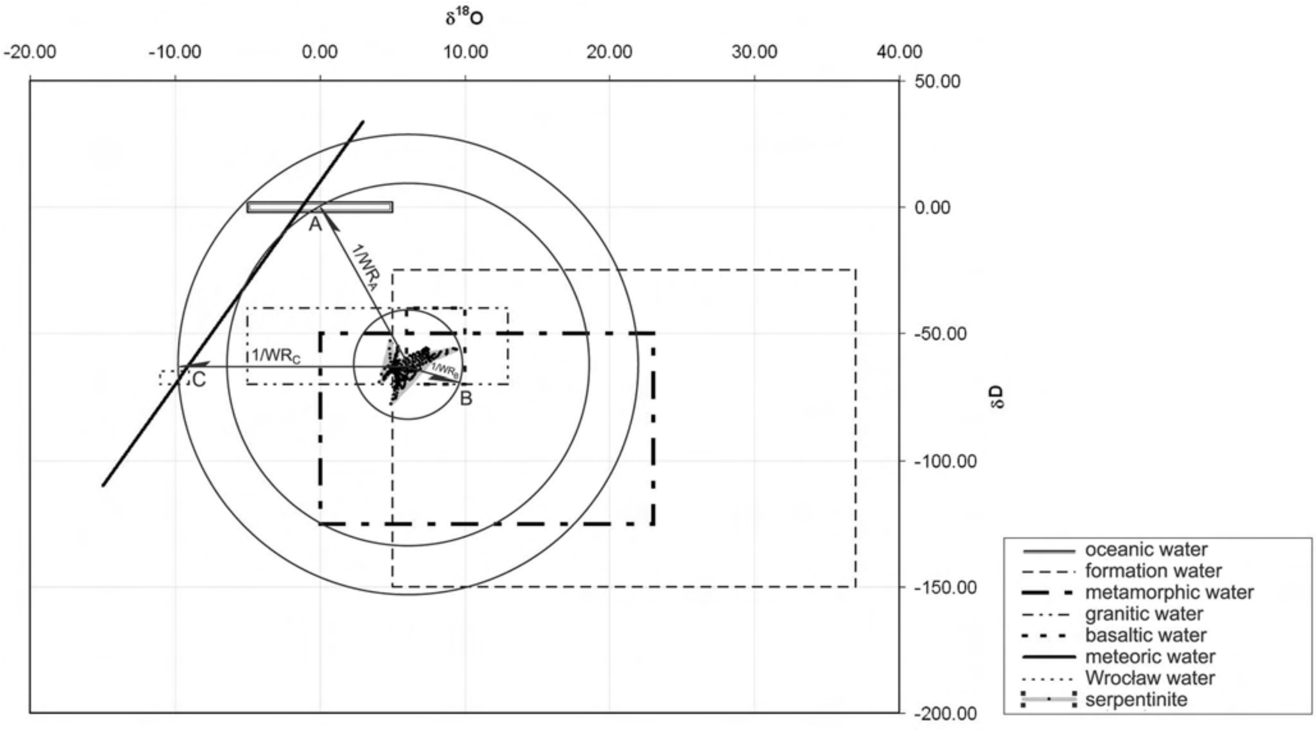
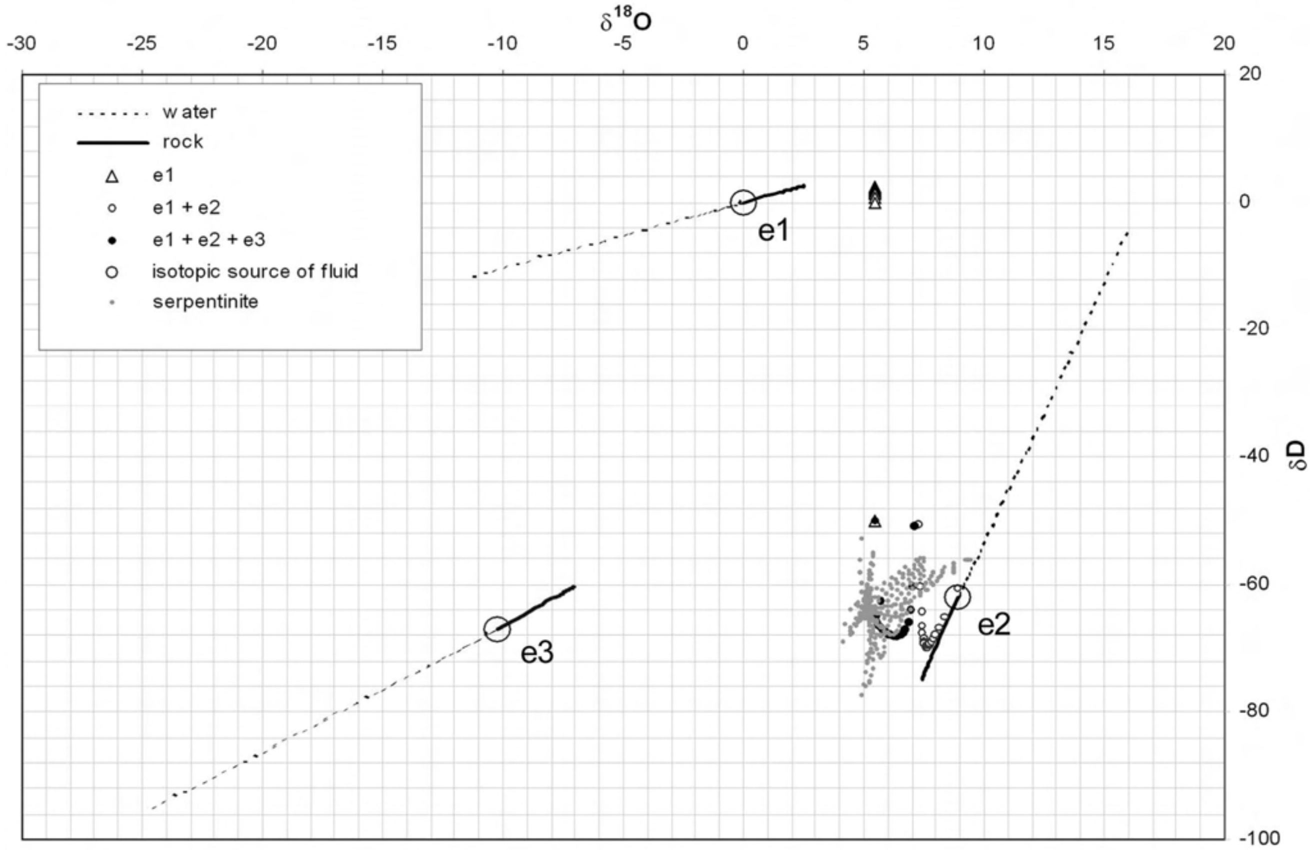


Fig. 6. Test of possibility to obtain the present values of oxygen and hydrogen isotopic composition in serpentinite through modification with alteration of three sources of serpentinizing fluids



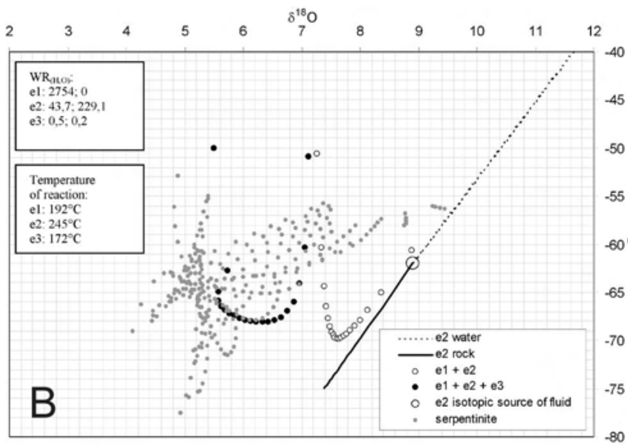


Fig. 7. **A** – isotopic fluid source in a 3-stage serpentinization model and model process of δD and δ^{18}O of the rock after each serpentinization stage, with fixed values of temperature and molar-to-rock ratio on the background of δD and δ^{18}O of serpentinite. Markers e1, e2 i e3 denote one-, two- and three-stages of serpentinization. Dashed and solid lines shows the changes δD and δ^{18}O of rock and water towards Rayleigh distillation; **B** – a part of Fig. 7a. Model process of δD and δ^{18}O of rock (e1 + e2 + e3) with fixed values of temperature and molar-to-rock ratio on the background of δD and δ^{18}O of serpentinite (*cf.* Fig. 8)

the fluids active in serpentinization, like, for instance, those of temperature or variability of δ^{18}O and δD of the rock along fluid migration paths.

δD and δ^{18}O values of the serpentinizing fluids in a 3-stage model of serpentinization of a selected migration path in the Gogołów–Jordanów Massif are plotted in Fig. 7. Temperatures of reaction and molar ratios W/R calculated with equation (3) are also given. The results are true for a migration path running from the south-eastern edge of the serpentinite massif towards its centre (Fig. 8).

Knowing molar relationships of each stage of serpentinization, it is possible to calculate the total mass of fluids active in metamorphic altering of the selected fragment of the Gogołów–Jordanów Massif.

INFLUENCE OF CO_2-BEARING FLUIDS ON THE CONTENT OF CARBONATES

Numerous authors tried to build models expressing the mode of rock-CO_2-bearing fluid interaction (Rye & Williams, 1981; Matsuhisa *et al.*, 1985; Zheng, 1990). Some models assume the balanced reactions fluid-rock (Zheng & Hoefs, 1993), what is not the case in the Gogołów–Jordanów Massif. However, none of the solutions known to the author accept differentiation of the isotopic δ^{13}C and δ^{18}O composition of the rock and fluid basing on the Rayleigh distillation. During an attempt of calculation of the mass of CO_2 and determining their source of origin, the same rules were used which accompanied modelling of the bulk flow of the fluid composed of water. Since the well-calibrated curve for carbon for magnesite-CO_2 is not known, the curve of isotopic fractionation, a, for of dolomite-CO_2 (Sheppard & Schwarcz, 1970; Ohmoto & Rye, 1979) was used, due to close resemblance of both curves (Weber-Weller, 2000; Gartzos, 2004). Moreover, the amount of carbonates within the rock was taken into account. Comparing the amounts of

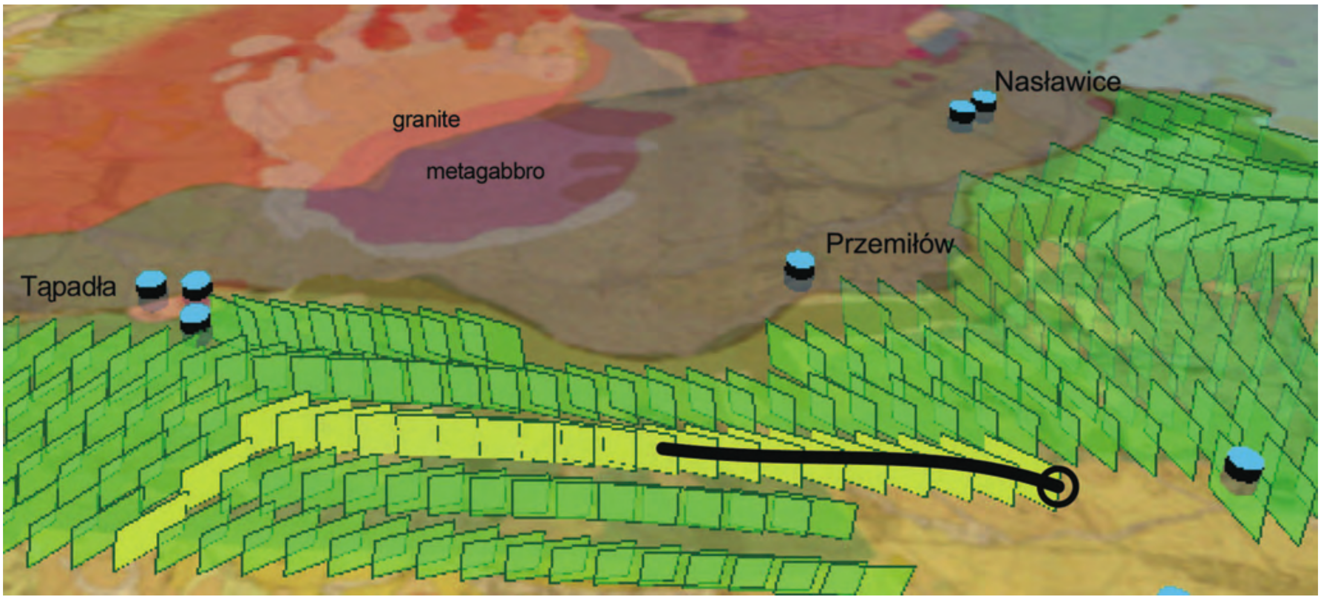


Fig. 8. The migration path arrangement of serpentinizing fluids (Fig. 7a) in the study area. The black line shows the point of entering fluid into the rock and range of influence on the rock

calcite and magnesite dispersed in the serpentine, it is likely to see that magnesite constitutes the main carbonate phase, particularly when the amount of carbonate minerals within serpentinite increases.

PATTERN OF TECTONIC STRESSES IN THE GOGOŁÓW–JORDANÓW MASSIF

The compressive stresses axis is oriented east-west and shows shallow plunge. Its orientation implies horizontal compression, oriented E–W to NE–SW in the SW part of the massif. The trajectories of s_1 stress mark the preferred strike orientation of extensional joints and faults, which are potential paths of fluid migration. Compression axes determined by the inversion method are, unlike those obtained from the NDA method, clearly deflected from the east-west orientation, and in the eastern part tend to parallel the serpentinite-gabbro boundary. On the other hand, the axis of tensional stress is nearly vertical, pointing to small thickness of the overburden during deformation. High values of R coefficients for the NDA method and F coefficients for the inversion method indicate considerable elongation of stress ellipsoids.

CONCLUSIONS

Isotopic analyses of oriented samples collected from the Gogołów–Jordanów Massif, together with measurements of planar structures and a computer-generated model of the channelised isotopic fluid-rock interaction, allow calculation of the isotopic mass balance. Basing on the variability of δD and δ^{18}O values for serpentinites along the paths of fluid migration it was found that serpentinization of peridotites was driven by fluids derived from at least three sources of different isotopic characteristics. The three following stages of serpentinization were distinguished that were assisted by oceanic, magmatic-hydrothermal and meteoritic waters.

1. The magmo-hydrothermal fluids played the dominant role in the serpentinization of peridotites since they constituted *ca*. 95% of the total mass of fluids, whereas the mass of oceanic water accounts to *ca*. 1% of the total mass of fluids.

2. To serpentinize 1 m^3 of rock, *ca*. $98 \cdot 10^4$ kg of fluid was necessary. The intensity of isotopic exchange between the fluid and the rock within a migration path, portrayed by the water-to-rock molar ratio, is strongly differentiated, and recalculated into the mass of fluid changes between $44 \cdot 10^3$ kg/m^3 to $56 \cdot 10^5$ kg/m^3 of the rock.

3. Strong differentiation in the intensity of isotopic exchange within a single migration path was observed: the activity of fluids diminishes with fluid migration along the path and sometimes drops to zero, leaving the rock unaltered.

4. Fluids bearing CO_2 most probably migrated vertically. The δ^{13}C values of dispersed magnesites point to a close relationship with endogenic sources. In the western part of the massif, δ^{13}C of dispersed magnesites attains a broader range of values compared to that of the eastern part, suggesting the influx of CO_2-bearing fluids from several feeding isotopic sources.

The compatibility of migration paths withthe trajectories of compressive stresses in the Gogołów–Jordanów Massif points to a decisive role of fractures and faults in the infiltration of serpentinizing fluids.

The presented results do not directly imply a tectonic setting for serpentinization. Instead, they allow estimation of a source of fluid that was apparently dominated by hydrothermal waters. This corollary does not necessarily mean that serpentinization occurred in a continental setting. Hydrothermal waters could have potentially altered the earlier isotopic composition of serpentinite acquired during sea-floor metamorphism. In such a case, the present isotopic composition would represent a later stage of hydratation that was active during and/or after obduction of the Ślęża ophiolite.

Acknowledgements

I would like to express my sincere thanks to the supervisors of my Ph.D. thesis, the selected portions of which are presented in this paper, namely to: Prof. Mariusz Orion Jędrysek and Prof. Stanisław Mazur, for their indispensable help, support and knowledge sharing. Prof. Stanisław Hałas and Prof. Piotr Gunia are gratefully thanked for their detailed reviews.

REFERENCES

Angelier, J., 1979. Determination of the mean principal directions of stresses for a given fault population. *Tectonophysics*, 56: 17–26.

Angelier, J. & Goguel, J., 1979. Sur une méthode simple de détermination des axes principaux des contraintes pour une population de failles. *C. R. Acad. Sci., Paris*, 288: 307–310.

Angelier, J. & Mechler, P., 1977. Sur une méthode graphique de recherche des contraintes principales également utilisable en tectonique et en séismologie: la méthode des dièdres droits. *Bulletin de la Societé Geologique de France*, VII, 19: 1309–1318; Paris.

Barnes, J. D., Selverstone, J. & Sharp, Z. D. 2004. Interactions between serpentinite devolatilization, metasomatism and strike-slip strain localization during deep-crustal shearing in the Eastern Alps. *Journal of Metamorphic Geology*, 22: 283–300.

Beaudoin, G. & Therrien, P., 2004. The web stable isotope fractionation calculator. In: De Groot, P. A. (*ed.*), *Handbook of stable isotope analytical techniques*, Volume I. Elsevier, Amsterdam: 1045–1047.

Birecki, T., 1962. Występowanie chromitów w Tąpadłach (In Polish). *Przegląd Geologiczny*, 3: 144–150.

Cymerman, Z., 1987. Związek ofiolitu Ślęży z waryscyjską strukturą metamorfiku sowiogórskiego. (In Polish). *Przegląd Geologiczny*, 35: 304–312.

Dubińska, E., Bylina, P., Kozłowski, A., Dörr, W., Nejbert, K., Schastok, J. & Kulicki, C., 2004. U-Pb dating of serpentinization: hydrothermal zircon from metasomatic rodingite shell (Sudetic ophiolite, SW Poland). *Chemical Geology*, 203: 183–203.

Duliński, M., Florkowski, T., Grabczak, J. & Różański, K., 2001. 25 lat systematycznych pomiarów składu izotopowego opadów na terenie Polski (In Polish). *Przegląd Geologiczny*, 49: 250–256.

Finckh, L., 1928. *Erläuterungen zur Geol. Karte von Preussen 1: 25 000. Blatt Zobten*. Berlin.

Floyd, P. A., Kryza, R., Crowley, Q. G., Winchester, J. A. & Abdel-Wahed, M. A., 2002. Ślęża ophiolite: geochemical features and relationship to Lower Palaeozoic rift magmatism in the Bohemian Massif. In: Winchester, J. A., Pharaoh, T. & Verniers, J. (eds), *Palaeozoic Amalgamation of Central Europe*, 201: 197–215.

Fyfe, W. S., Price, N. J. & Thompson, A. B., 1978. *Fluids in Earth's Crust*. Elsevier, Amsterdam.

Gartzos, E., 2004. Comparative stable isotopes study of the magnesite deposits of Greece. *Bulletin of the Geological Society of Greece*, 36: 196–203.

Graham, C. M., Sheppard, S. M. F. & Heaton, T. H. E., 1980. Experimental hydrogen isotope studies: I. Systematics of hydrogen isotope fracionaction in the systems epidote-H_2O, zoisite-H_2O and $AlO(OH)$-H_2O. *Geochimica et Cosmochimica Acta*, 44: 353–364.

Graham, C. M., Viglino, J. A. & Harmon, R. S., 1987. Experimental study of hydrogen-isotope exchange between aluminous chlorite and water and of hydrogen diffusion in chlorite. *American Mineralogist*, 72: 566–579.

Gunia, P., 1989. Spinele chromowe ze wzgórza "Czarna Góra" jako wskaźniki petrogenezy ultrabazytów zespołu ofiolitowego grupy górskiej Ślęży (In Polish). In: *Ofiolit Ślęży i jego mineralizacja rudna, Wrocław-Sobótka, 4-8 września 1989*. Instytut Nauk Geologicznych Uniwersytetu Wrocławskiego, Państwowy Instytut Geologiczny – Oddział Dolnośląski, Polskie Towarzystwo Geologiczne. Wydawnictwo Uniwersytetu Wrocławskiego, Wrocław: 141–150.

Hoefs, J., 1996. *Stable Isotope Geochemistry*. Springer – Verlag, Berlin, 201 pp.

Jędrysek, M. O., 1985. *Budowa geologiczna zespołu ofiolitowego Ślęży* (In Polish). Unpublished M.Sc. thesis, Institute of Geological Sciences, University of Wrocław, Wrocław.

Jędrysek, M. O., 1989. Hydrogen, carbon, and oxygen isotope model of serpentinization of ultramafic rocks exemplified by Ślęża and Braszowice complexes. In: Narębski, W. & Majerowicz, A. (*eds*), *Lower and Upper Palaeozoic Metabasites and Ophiolites of Polish Sudetes*. Multilateral Cooperation of Academies of Sciences of Socialist Countries, Problem Commission IX, Earth's Crust Structure Evolution, Metallogeny, Guidebook of Excursions in Poland, p. 73–91.

Jędrysek, M. O. & Hałas, S., 1989. $\delta^{13}C$ and $\delta^{18}O$ evidence for magmatic origin of calcite contained in ultramafic cumulates from Tapadla; Ślęża ophiolite complex, SW Poland. *Mineralogica Polonica*, 20: 3–9.

Jędrysek, M. O. & Sachanbiński, M., 1994. Stable isotope and trace elements studies of vein ophicarbonates at Gogolów–Jordanów Serpentinite Massif (Poland): a contribution to the origin of ophiaragonite and ophimagnesite. *Geochemical Journal*, 28: 341–350.

Łomnicki, A., 1999. *Wprowadzenie do statystyki dla przyrodników*. (In Polish). Wydawnictwo Naukowe PWN, Warszawa.

Majerowicz, A., 1979. Grupa górska Ślęży a współczesne problemy petrologiczne ofiolitów (In Polish). In: Materiały konferencji terenowej: *Wybrane zagadnienia stratygrafii, petrografii i tektoniki wschodniego obrzeżenia gnejsów sowiogórskich i metamorfiku kłodzkiego*. Wydawnictwo Uniwersytetu Wrocławskiego, Wrocław: 9–34.

Majerowicz, A., 1981. Rock series of Ślęża Mt. group in the light of ophiolite complexes. In: Narębski, W. (*ed.*), *Ophiolites and initialites of northern border of the Bohemian Massif*. Guidebook of Excursion 2, Potsdam-Freiberg: 172–179.

Majerowicz, A., 1984. Petrography and genesis of rodingites in serpentinites of the Ślęża ophiolitic group. (In Polish, English summary). *Geologia Sudetica*, 18: 110–130.

Majerowicz, A., 1995. Zarys geologii (In Polish). *Przyroda Ślężańskiego Parku Krajobrazowego. Informator*. Ślężański Park Krajobrazowy, Sobótka: 10–15.

Majerowicz, A., 2006. *Krótki przewodnik terenowy po skałach ofiolitowego zespołu Ślęży oraz ich petrologicznej i geologicznej historii*. (In Polish). Wydawnictwo Uniwersytetu Wrocławskiego, Wrocław: 1–64.

Majerowicz, A. & Pin, C., 1986. Preliminary trace element evidence for an oceanic depleted mantle origin of the Ślęża ophiolitic complex, SW Poland. *Mineralogica Polonica*, 17: 13–22.

Majerowicz, A. & Pin, C., 1989. Recent progress in petrologic study of the Ślężą ophiolite complex. In: Narębski, W. & Majerowicz, A. (*eds*), *Lower and Upper Palaeozoic metabasites and ophiolites of the Polish Sudetes. Guide book of excursions in Poland*. Uniwersytet Wrocławski, Wrocław: 4–72.

Majerowicz, A. & Pin, C., 1994. The main petrological problems of the Mt. Ślęża ophiolite complex, Sudetes, Poland. *Zentralblatt für Geologie und Paläontologie*, 1: 989–1018.

Majerowicz, A., Kryza, R. & Wróblewska, G., 2000. Diallagite pegmatitoids from Mt. Ślęża gabbro. In: Mierzejewski, M. P. (*ed.*), *Tectonics of the Ślęża ophiolite and its influence on the distribution of some mineral ores and groundwater*. Uniwersytet Wrocławski, Instytut Nauk Geologicznych, Wrocław: 49–54.

Malthe-Sørenssen, A., Jamtveit, B. B. & Meakin, P. 2006. Fracture patterns in chemical decomposition of solids. *Physical Review Letters*, 96: 245–501.

Masters, R. L. & Ague, J. J., 2005. Regional-scale fluid flow and element mobility in Barrow's metamorphic zones, Stonehaven, Scotland. *Contributions to Mineralogy and Petrology*, 150: 1–18.

Matsuhisa, Y., Morishita, Y. & Sato, T., 1985. Oxygen and carbon isotope variations in gold-bearing hydrothermal veins in the Kushikino mining area, southern Kyushu, Japan. *Economic Geology*, 80: 283–293.

Mierzejewski, M. P. & Abdel-Wahed, M. A., 2000. Overlapping thrust faults within the Gogołów–Jordanów serpentinite massif. In: Mierzejewski, M. P. (*ed.*), *Tectonics of the Ślęża ophiolite and its influence on the distribution of some mineral ores and ground water*. Uniwersytet Wrocławski, Instytut Nauk Geologicznych, Wrocław: 29–48.

Mydłowski, A., 2006. An application of the water-to-rock molar ratio for calculating the amount and composition of metamorphic fluids with regard to Rayleigh distillation. *Mineralogical Society of Poland – Special Papers*, 29: 228–231.

Mydłowski, A. & Jędrysek, M. O., 2004. Nowe rozwiązania w badaniach nad etapami przeobrażeń kompleksów ofiolitowych w Sudetach. (In Polish). In: *Zagadnienia interdyscyplinarne w górnictwie i geologii IV Krajowa Konferencja Doktorantów*, *Szklarska Poręba, 29-31 stycznia 2004 r*.

Narębski, W., Wajsprych, B. & Bakun-Czubarow, N., 1982. On the nature, origin and geotectonic significance of ophiolites and related rock suites in the Polish part of the Sudetes. *Ofioliti*, 7, 2/3: 407–428.

Oberc, J., 1972. Sudety i obszary przyległe. (In Polish). In: *Budowa geologiczna Polski*, T. IV, *Tektonika*, cz. 2. Wydawnictwa Geologiczne, Warszawa, 276 pp.

Ohmoto, H. & Rye, R. O., 1979. Isotope of sulfur and carbon. In: Barnes, H. L. (*ed.*), *Geochemistry of Hydrothermal Deposits*. John Wiley & Sons, Chichester: 509–567.

Oliver, G. J. H., Corfu, F. & Hrogh, T. E., 1993. U-Pb ages from SW Poland: evidence for Caledonian suture zone between Baltica and Gondwana. *Journal of Geological Society, London*, 150: 355–369.

Oliver, N. H. S., 1996. Review and classification of structural controls on fluid flow during regional metamorphism. *Journal of Metamorphic Geology,* 14: 477–492.

Ord, A. & Oliver, N. H. S., 1997. Mechanical controls on fluid flow during regional metamorphism: some numerical models. *Journal of Metamorphic Geology,* 15: 345–359.

Pin, C., Majerowicz, A. & Wojciechowska, I., 1988. Geochemia pierwiastków śladowych i izotopów strontu i neodymu ofiolitowych masywów Nowej Rudy i Ślęży. (In Polish). In: *Petrologia i geologia fundamentu waryscyjskiego polskiej części Sudetów*. Wrocław 11-13.09.1988.

Quenardel, J. M., Brochwicz-Lewiński, W., Cymerman, Z., Grocholski, A., Kossowska, I., Pique, A. & Ploquin, A., 1988. The Polish Sudetes: a mosaic of Variscan terranes. *Trabajos de Geologia*, 17: 139–144.

Rayleigh, J. W., 1896. Theoretical considerations respecting the separation of gases by diffusion and similar processes. *Philosophical Magazine*, 42: 1–493.

Rye, D. M. & Williams, N., 1981. Studies of the base metal sulfide deposits at McArthur River, Northern Territory, Australia: III. The stable isotope geochemistry of the H.Y.C. Ridge and Cooley deposits. *Economic Geology*, 76: 1–26.

Saccocia, P. J., Seewald, J. S. and Shanks, W. C., 2001. New D–H and ^{18}O–^{16}O fractionation factors for serpentine and talc from 250 to 450 °C. *Eos, Transactions of the American Geophysical Union*, 82 (47), Fall Meeting Supplement.

Sachanbiński, M., 1984. Zespoły mineralne z kopalni magnezytu Wiry w Wirach (In Polish). In: *Mineralogia i tektonika masywu granitoidowego Strzegom-Sobótka. Materiały Konferencji Naukowej, Strzegom 28-29.09.1984*. Wydawnictwo Uniwersytetu Wrocławskiego, Wrocław: 112–118.

Sakai, H. & Tsutsumi, M., 1978. D/H fractionation factors between serpentine and water at 100° to 500° and 2000 bar water pressure and the D/H ratios of natural serpentines. *Earth and Planetary Science Letters*, 40: 231–242.

Satake, H. & Matsuo, S., 1984. Hydrogen isotopic fractionaction factor between brucite and water in the temperature range from 100°C to 510°C. *Contributions to Mineralogy and Petrology*, 86: 19–24.

Sheppard, S. M. F. & Schwarcz, H. P., 1970. Fractionation of carbon and oxygen isotopes and magnesium between coexisting metamorphic calcite and dolomite. *Contributions to Mineralogy and Petrology*, 26: 161–198.

Spang, J. H., 1972. Numerical Method for Dynamic Analysis of Calcite Twin Lamellae. *Geological Society of America Bulletin*, 83: 467–472.

Spangenberg, K., 1943. Die Chromerzlagerstätte von Tampadel am Zobten. *Zeitschrift für praktische Geologie,* 51: 13–35.

Sverjensky, D. A., 1981. Isotopic alteration of carbonate host rocks as a function of water to rock ratio – An example from the Upper Mississippi Valley zinc-lead district. *Economic Geology*, 76: 154–157.

Taylor, H. P., 1974. The application of oxygen and hyrogen isotope studies to problems of hydrothermal alteration and ore deposition. *Economic Geology*, 69: 843–883.

Taylor, H. P., 1977. Water/rock interactions and the origin of H_2O in granitic batholiths. *Journal of the Geological Society*, 133: 509–558, Scottish Academic Press Ltd.

Teisseyre, H., Smulikowski, K. & Jahn, A., 1960. *Regionalna Geologia Polski*, T. III. *Sudety*, z. 2, *Utwory trzeciorzędowe i czwartorzędowe oraz pogląd na rozwój budowy geologicznej Sudetów*. Polskie Towarzystwo Geologiczne, Kraków: 303–438.

Thompson, A. B., 1987. Some aspects of fluid motion during metamorphism. *Journal of the Geological Society*, 144: 309–312.

Valley, J. W. & Cole, D. R. (*eds*), 2001. Stable Isotope Geochemistry. *Reviews in Mineralogy & Geochemistry*, 43: 662 pp. Mineralogical Society of America, Washington, D.C.

Vollmer, R., 1976. Rb-Sr and U-Th-Pb systematics of alkaline rocks: the alkaline rocks from Italy. *Geochimica et Cosmochimica Acta*, 40: 283–295.

Watt, G. R., Oliver, N. H. S. & Griffin, B. J., 2000. Evidence for reaction-induced microfracturing in granulite facies migmatites. *Geology*, 28: 327–330.

Weber-Weller, A., 2000. *Termodynamiczne i kinetyczne efekty* *izotopowe w ewolucji skał zespołów ofiolitowych Ślęży i Nowej Rudy* (In Polish). Unpublished Ph.D. thesis, Institute of Geological Sciences, University of Wrocław, Wrocław, 117 ms. pp.

Wenner, D. B. & Taylor, H. P., 1973. Oxygen and hydrogen isotope studies of the serpentinization of ultramafic rocks in oceanic environments and continental ophiolite complexes. *American Journal of Science*, 207: 207–239.

Winchester, J. A. & PACE TMR Network Team, 2002. Palaeozoic amalgamation of Central Europe: new results from recent geological and geophysical investigations. *Tectonophysics*, 360: 5–21.

Zheng, Y. F., 1990. Carbon-oxygen isotopic covariation in hydrothermal calcite during degassing of CO_2: a quantitative evaluation and application to the Kushikino gold mining area in Japan. *Mineralium Deposita*, 25: 246–250.

Zheng, Y. F. & Hoefs, J., 1993. Carbon and oxygen isotopic covariations in hydrothermal calcites. *Mineralium Deposita*, 28: 79-89.

Znosko, J., 1981. The problem of oceanic crust and of ophiolites in the Sudetes. In: Narębski, W. (*ed.*), *Ophiolites and Initialites of Northern Border of the Bohemian Massif. Guidebook of Excursions, May–June 1981*. Vol. II. Potsdam: 3–28.