

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

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**Abstract:** This work aims at estimation of the amount of metamorphic fluids which led to the present-day variability of isotopic compositions,  $\delta D$  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  $\delta D$  and  $\delta^{18}O$  in the serpentinites along the modelled migration paths demonstrates that serpentinitization 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 serpentinitization, since they represent approximately 95% of all fluids interacting with the rock. In contrast, oceanic water represents only 1% of fluids involved in serpentinitization. The calculated mean amount of fluid required for serpentinitization of 1 m<sup>3</sup> of peridotite is equal to  $98 \cdot 10^4$  kg.

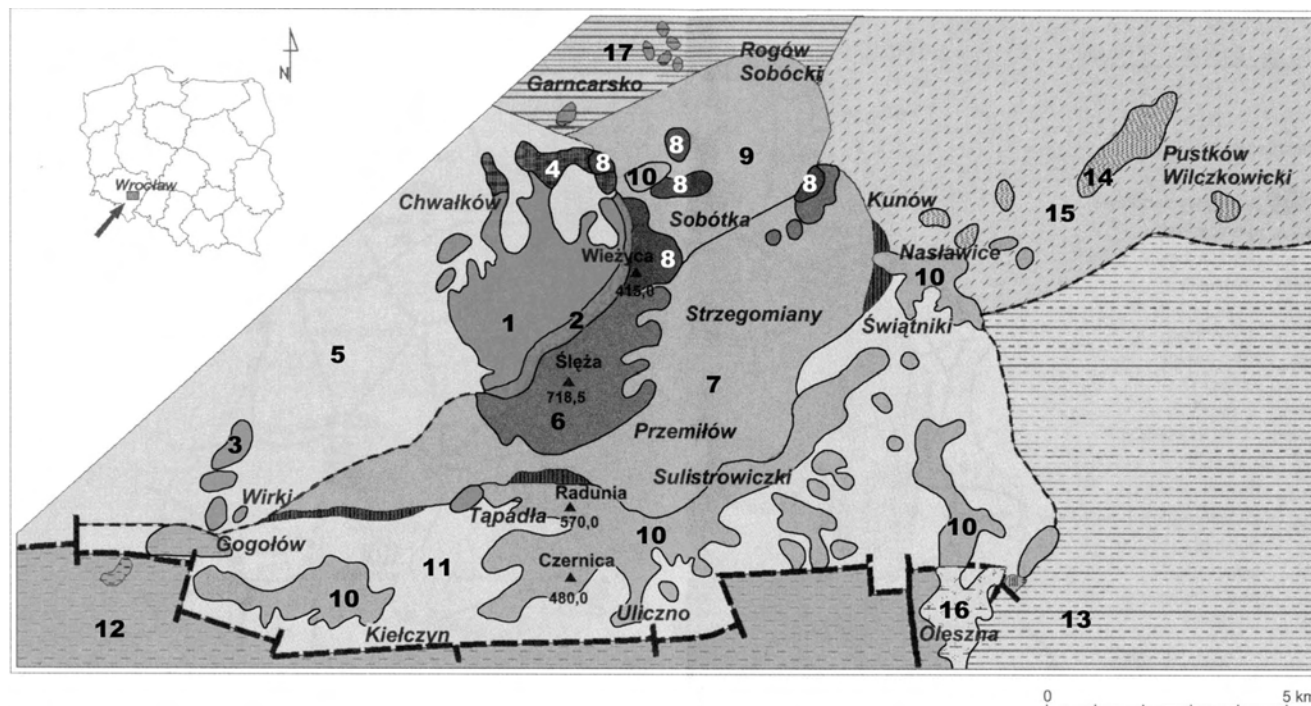
**Key words:** serpentinitization, stable isotope, tectonics, numerical modelling, Gogołów–Jordanów Massif, Lower Silesia, SW Poland.

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### INTRODUCTION

For the last thirty years the vast amount of work has been done to document the origin, evolution and tectonic position of the Ślęza ophiolite complex (Majerowicz, 2006 and references therein). Consequently, there is no doubt today that the Ślęza 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 serpentinitization that affected the ultramafic member of the Ślęza ophiolite. Uncertain is the source of serpentinitizing 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 serpentinitization of ultramafic rocks and dehydration 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 hydration, resulting in local perturbations of the stress field (*e.g.*, Watt *et al.*, 2000; Malthe-Sørensen *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 Ślęza 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 Gogolów–Jordanów massif, 11 – serpentinites, covered, 12 – gneisses of the Góry Sowie Mts., 13 – gneisses of the eastern cover of the Ślęza Massif, 14 – phyllites, epimetamorphic greywacke and siliceous schists, 15 – phyllites, epimetamorphic greywacke and siliceous 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 Gogolów–Jordanów serpentinite massif was created to reconstruct the migration of fluids responsible for serpentinitization. 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

### Ślęza Ophiolite Complex

Mafic and ultramafic rocks in the vicinity of the Ślęza Mt. form a nearly complete ophiolite association including serpentinitized 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 Ślęza 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 Ślęza 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  $\delta D$  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 Ślęza ophiolite preclude their affiliation to one coherent ophiolitic suite.

The Ślęza 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 Ślęza ophiolite represents a vestige of oceanic crust (Majerowicz, 1979, 1981; Narebski *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 serpentinites 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 Ślęza 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 Ślęza ophiolite has been dated at  $400 \pm 3$  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 Ślęza gabbro, the protolith of which was dated at *ca.* 420 Ma (Oliver *et al.*, 1993). The whole rock Sm-Nd age of  $353 \pm 21$  Ma, obtained for the Ślęza ophiolite by Pin *et al.* (1988), presumably corresponds to metamorphism or cooling of the ophiolite complex.

The Gogołów–Jordanów Massif consists of serpentinized ultramafic rocks that crop out in the area of  $90 \text{ km}^2$ . 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-coloured, 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 Tapadła 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 transform 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 Wrocław, 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 strata, as well as isotopic analyses of oriented samples.

Taking into account complicated geological structure and the lack of possibilities 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  $\alpha_i$  and dip  $\beta_i$ , the coefficients  $x_i, y_i, z_i$  were determined:

$$\begin{aligned} x_i &= \cos \alpha_i \sin \beta_i \\ y_i &= \sin \alpha_i \sin \beta_i \\ z_i &= \cos \beta_i \end{aligned} \quad (1)$$

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

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

Determination of the average value of angle  $\gamma$  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 dihedral 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  $\Delta$  value and vice versa. It is also possible to read temperatures at a given value of  $\alpha$ , *i.e.* the coefficient of isotopic fractionation basing on a selected curve for a known temperature. Interactive plot of  $\alpha$  vs.  $t^\circ\text{C}$  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  $\delta\text{D}$  and  $\delta^{18}\text{O}$  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 unknown values. The base of determination of the water-to-rock ratio is the set of values of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  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  $\delta\text{D} - \delta^{18}\text{O}$  values of the rock and a given point on the surface of the study area. Using an iterative technique, the shape of curvature of the model variability of  $\delta\text{D} - \delta^{18}\text{O}$  was applied to the real course of  $\delta\text{D} - \delta^{18}\text{O}$  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  $\delta\text{D}$  and  $\delta^{18}\text{O}$ , 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 serpentinizing 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 ( $\delta\text{D}$ ) of serpentinite rocks vary from  $-102.3\text{‰}$  to  $-13.4\text{‰}$ , whereas those of the Ślęża gabbros bordering from the north the Gogołów–Jordanów Massif range between  $-49.6\text{‰}$  and  $-2.9\text{‰}$ . The highest values of  $\delta^{18}\text{O}$  of serpentine attains  $11.15\text{‰}$ , the lowest is  $1.45\text{‰}$ . For the gabbros, the  $\delta^{18}\text{O}$

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  $\Delta$  ( $\delta_{\max} - \delta_{\min}$ ) 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

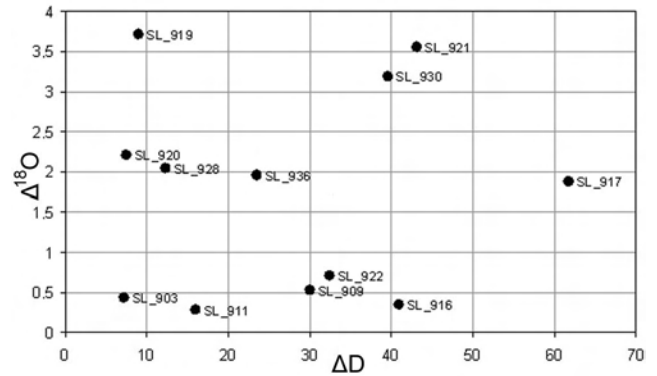
Before incorporating hydrogen particles from the fluid into ultramafic rock during serpentinization, the water-to-rock molar ratio (W/R) should be close to infinity for the hydrogen, and after the reaction is finished it should approach zero (all hydrogen reacted with the rock). However, the hitherto 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 ( $\infty:0$ ).

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):

$$\frac{W}{R} = \frac{\left( \frac{f}{r_{rz}} \frac{i}{r_{rz}} \right)}{\left( \frac{i}{w} \frac{f}{r_{rz}} \right)} \quad (3)$$

where:

- $\delta_{r_{rz}}^i, \delta_{r_{rz}}^f$  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).

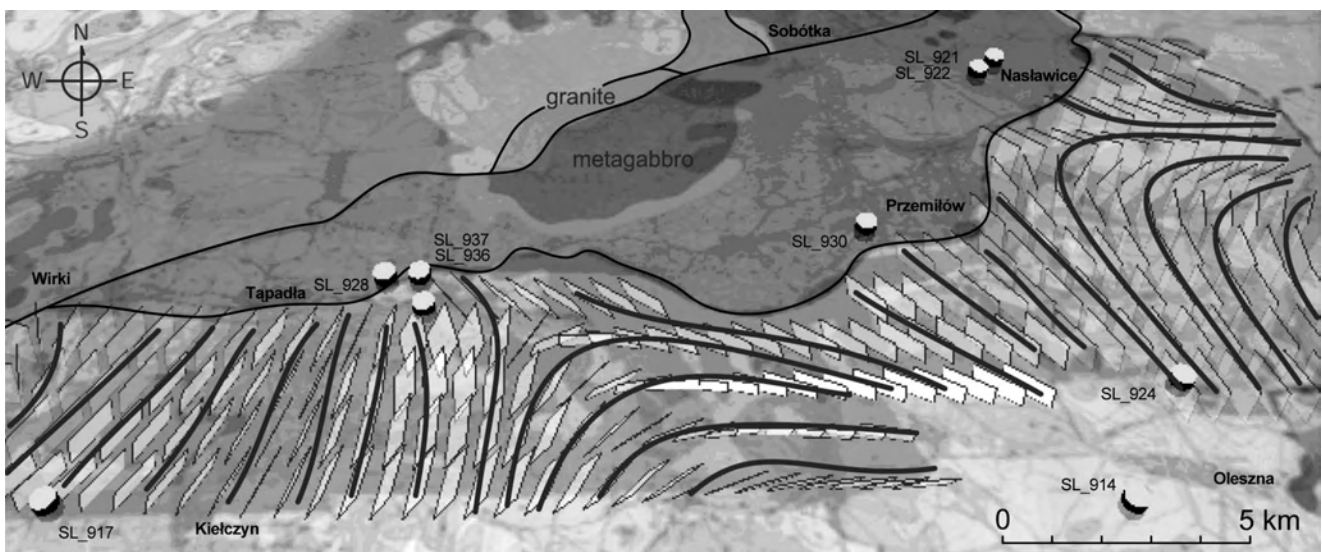


**Fig. 2.** Comparison of  $\Delta$  ( $\delta_{\max} - \delta_{\min}$ ) hydrogen and oxygen values in the serpentine between oriented samples at the single outcrop scale

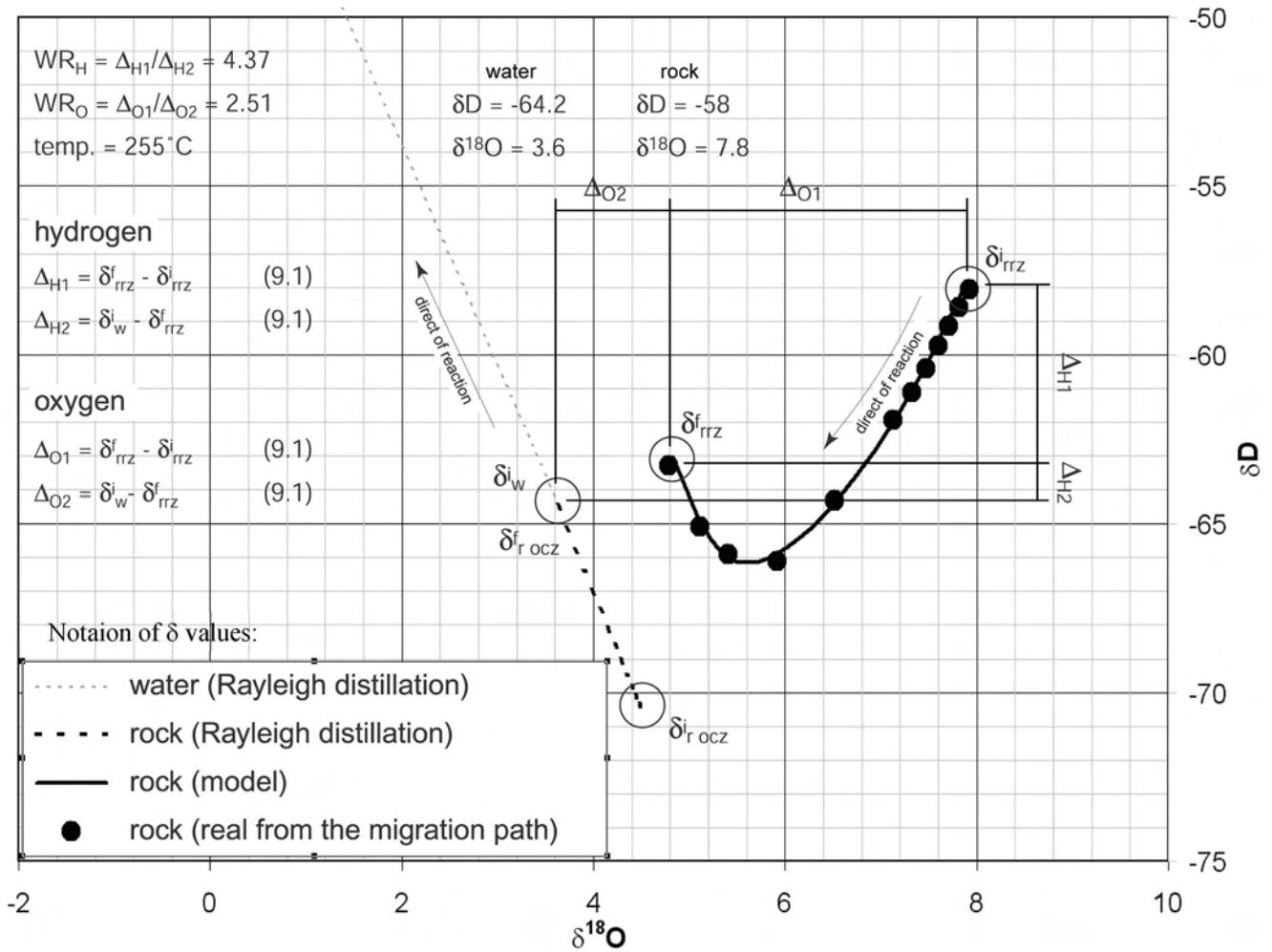
The water-to-rock molar ratio will attain values derived from a set of real positive values. Knowing W/R values before the isotope exchange reaction starts is of crucial importance in estimating the amount of fluid reacting with the rock and its further influence on metamorphism.

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  $\delta D$  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  $\delta D - \delta^{18}O$  space with marked initial isotopic composition of the rock, variability  $\delta D$  and  $\delta^{18}O$  of rock from selected migration path, and adjusted to model  $\delta D$  and  $\delta^{18}O$  of the rock. Explanations:  $\delta_{rrz}^i, \delta_{rrz}^f$  – initial and final real isotopic composition of rock, respectively – isotopic composition from the rock-sample measured;  $\delta_w^i$  – initial isotopic composition of fluid = final expected isotopic composition of rock (final isotopic composition of rock according to Rayleigh distillation);  $\delta_{r\ ocz}^i$  – initial expected isotopic composition of rock;  $\delta_{r\ ocz}^f$  – final expected isotopic composition of the rock

### One-stage serpentinization

The aim of one-stage modelling of serpentinization of the Gogolów–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 ( $\delta D$  and  $\delta^{18}O$ ) 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).

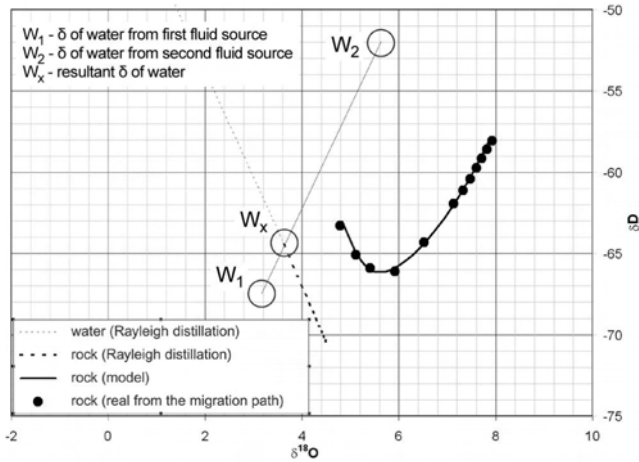
### Two-stage serpentinization

A two-stage model of serpentinization should enable the reaction of rock masses with two fluids of any isotopic composition ( $\delta D, \delta^{18}O$ ), temperature, and the amount of ( $W/R_{(H_2O)}$ ). 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 ( $\delta D, \delta^{18}O$ ) to the present-day state (reverse modelling), keeping the  $\delta D$  and  $\delta^{18}O$  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 ( $\delta D, \delta^{18}O$ ) to changes resulting from  $\delta D$  and  $\delta^{18}O$  of water, temperature of reaction, and molar ratios  $W/R_{(H_2O)}$  for several consecutive stages. It is associated with the influence, on the same rock mass, of several, consecutive serpentinizing fluids of variable isotopic composition ( $\delta D, \delta^{18}O$ ), different temperature, and the amount of ( $W/R_{(H_2O)}$ ). Fluid of the following, younger stage modifies isotopic



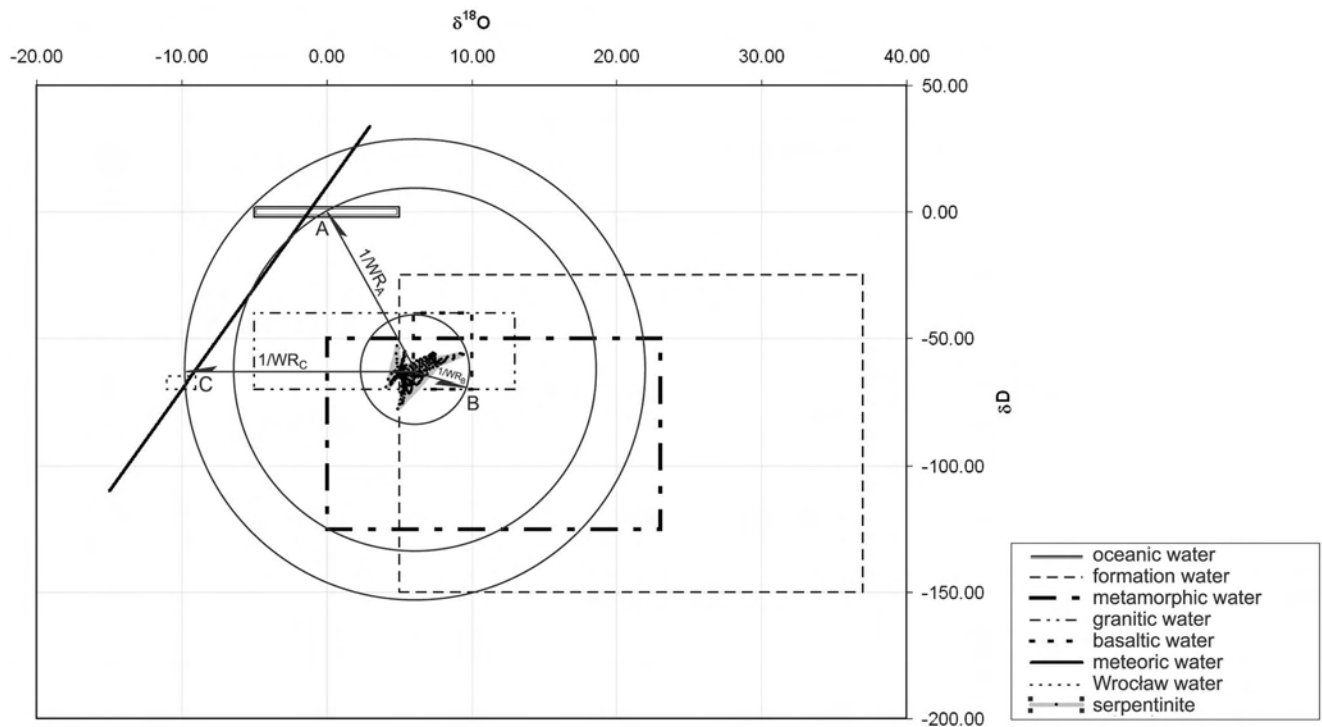
**Fig. 5.** Arrangement of two fluid sources with respect to hypothetical fluid source determined in one-stage serpentinization model

composition of the rock, already altered by fluids active during previous stages of serpentinization. In this sense, the molar ratio  $W/R_{(\text{H}_2\text{O})}$  acquires a new meaning, constraining molar proportions of water from a given stage of serpentinization in respect to the rock altered by previous fluids.

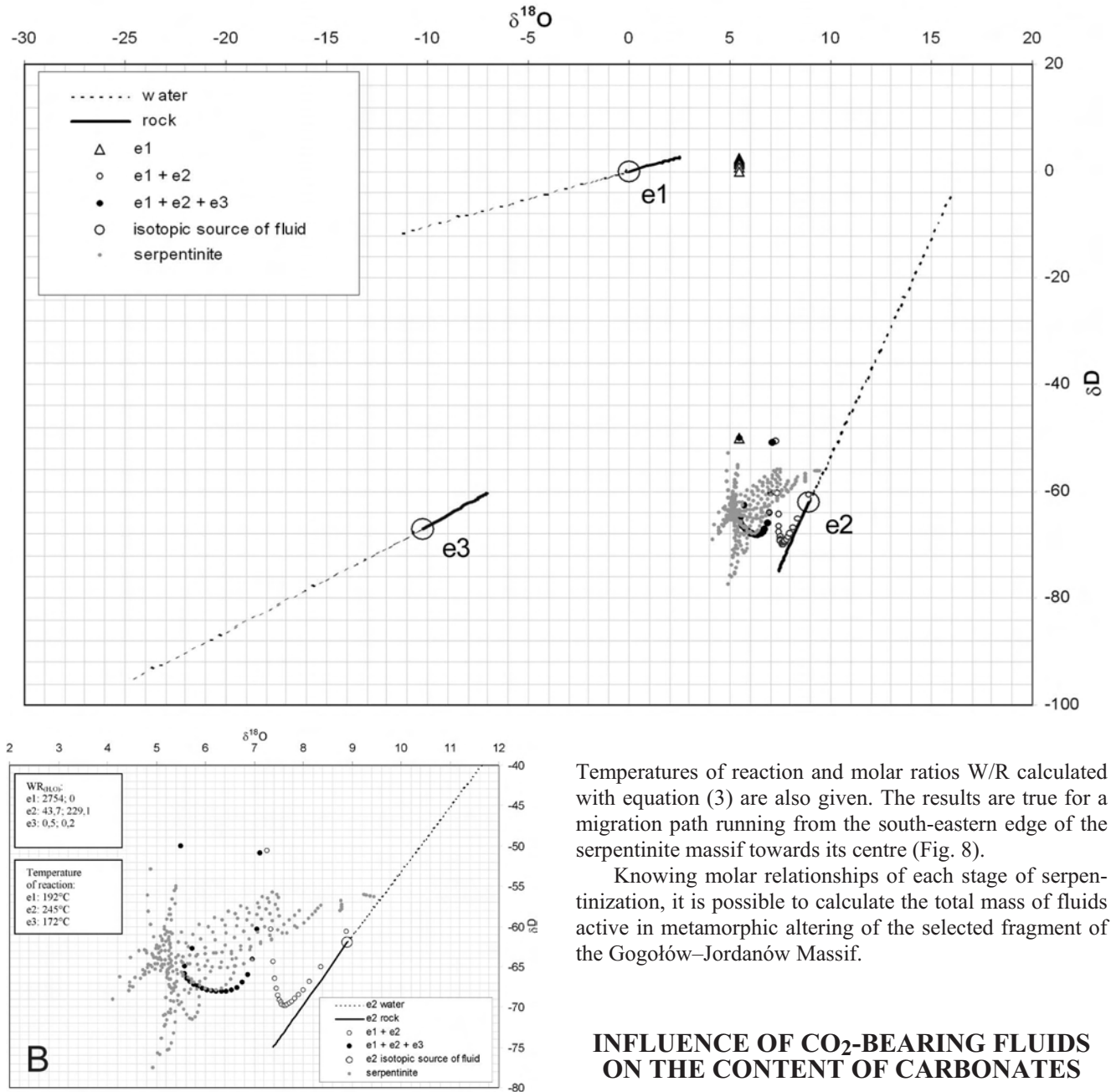
The basic task preceding multi-stage modelling consists in verifying whether the presence of at least three fluids is sufficient for changing isotopic composition ( $\delta\text{D}$ ,  $\delta^{18}\text{O}$ ) of ultramafic rock to the present-day state (reverse modelling), maintaining at the same time the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of de-

livery 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 ( $\delta\text{D}$ ,  $\delta^{18}\text{O}$ ), whose deviation ( $\Delta\text{D}$ ,  $\Delta^{18}\text{O}$ ) 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  $\Delta\text{D}/\Delta^{18}\text{O}$  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 ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) of serpentine, 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  $\delta^{18}\text{O}$  and  $\delta\text{D}$  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  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in serpentine, 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  $\delta\text{D}$  and higher  $\delta^{18}\text{O}$  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  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , typical for serpentine. 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 serpentine 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  $\delta D$  and  $\delta^{18}O$  of the rock after each serpentinization stage, with fixed values of temperature and molar-to-rock ratio on the background of  $\delta D$  and  $\delta^{18}O$  of serpentinite. Markers e1, e2 i e3 denote one-, two- and three-stages of serpentinization. Dashed and solid lines shows the changes  $\delta D$  and  $\delta^{18}O$  of rock and water towards Rayleigh distillation; **B** – a part of Fig. 7a. Model process of  $\delta D$  and  $\delta^{18}O$  of rock (e1 + e2 + e3) with fixed values of temperature and molar-to-rock ratio on the background of  $\delta D$  and  $\delta^{18}O$  of serpentinite (*cf.* Fig. 8)

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

$\delta D$  and  $\delta^{18}O$  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.

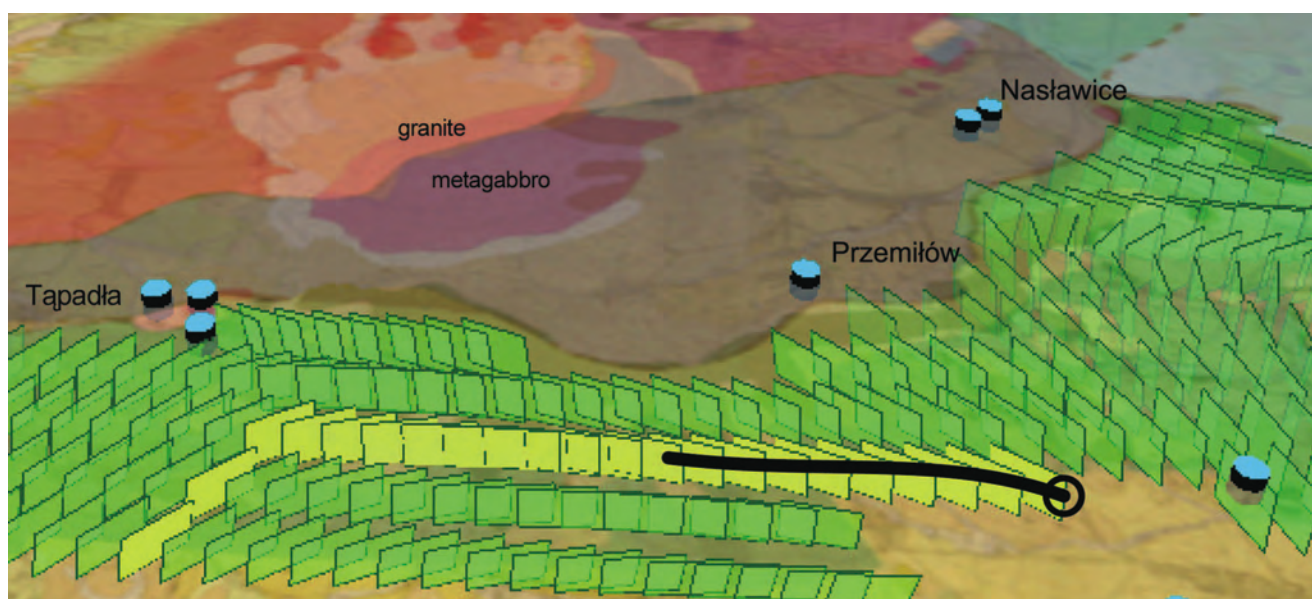
Temperatures of reaction and molar ratios W/R calculated with equation (3) are also given. The results are true for a migration path running from the south-eastern edge of the serpentinite massif towards its centre (Fig. 8).

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<sub>2</sub>-BEARING FLUIDS ON THE CONTENT OF CARBONATES

Numerous authors tried to build models expressing the mode of rock-CO<sub>2</sub>-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  $\delta^{13}C$  and  $\delta^{18}O$  composition of the rock and fluid basing on the Rayleigh distillation. During an attempt of calculation of the mass of CO<sub>2</sub> 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<sub>2</sub> is not known, the curve of isotopic fractionation, a, for of dolomite-CO<sub>2</sub> (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  $\delta D$  and  $\delta^{18}O$  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 fol-

lowing 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  $1 \text{ m}^3$  of rock, *ca.*  $98 \cdot 10^4 \text{ kg}$  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  $44 \cdot 10^3 \text{ kg/m}^3$  to  $56 \cdot 10^5 \text{ kg/m}^3$  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  $\text{CO}_2$  most probably migrated vertically. The  $\delta^{13}\text{C}$  values of dispersed magnesites point to a close relationship with endogenic sources. In the western part of the massif,  $\delta^{13}\text{C}$  of dispersed magnesites attains a broader range of values compared to that of the eastern part, suggesting the influx of  $\text{CO}_2$ -bearing fluids from several feeding isotopic sources.

The compatibility of migration paths with the 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 hydration that was active during and/or after obduction of the Ślęża ophiolite.

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