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CARBONATES IN MÉLANGES FROM RZESZÓWEK AND STANISŁAWÓW (KACZAWA COMPLEX, SUDETES): CHEMICAL, XRD AND CL INVESTIGATIONS

Abstract: Carbonates have been identified in mélange-type deposits at Stanislawów and Rzeszówek in the northern part of the Kaczawa Complex using XRD, CL and EDS methods. Their chemistry, as revealed by WDS, shows great similarity to that of carbonates of recent accretionary prisms, drilled during the ODP programme. The studied carbonates divided into two groups: 1) phases intermediate between siderite and magnesite, 2) phases with a mixed dolomite-ankerite and rarely calcite composition. The Kaczawa Complex is regarded as a fragment of a Variscan accretionary prism and the presence of these carbonate phases is consistent with this hypothesis.

Keywords: Ca-Mg-Fe carbonates, Fe-Mg-Mn carbonates, mélange, accretionary prism, Kaczawa Complex, Sudetes

INTRODUCTION

Mélange-type deposits occur in the northern part of the Kaczawa Mountains (W Sudetes; Baranowski et al. 1998, Collins et al. 2000). They were encountered in boreholes near Stanislawów (Chelmiec Unit) and in the profile along the Kamiennik stream at Rzeszówek (Rzeszówek-Jakuszowa Unit). The origin of the Kaczawa mélanges is generally related to the formation and evolution of the Variscan accretionary prism, of which the Kaczawa Complex is now thought to be a part. Many features of these rocks resemble recent accretionary prism deposits, e.g. drilled within the framework of the Ocean Drilling Program (ODP; Collins et al. 2000). Considerable attention has recently been focused on the authigenic carbonates contained within the sediments of the accretionary prisms (Rad et al. 1996, Deyhle et al. 2001, Carson et al. 2003). The process of their origin may be roughly envisaged as proceeding in two steps: 1) decomposition of organic matter to methane and CO_2 in the course of diagenetic transformations caused by bacteria as well as by increasing temperature and pressure resulted from tectonic compaction, 2) formation of carbonates as the products of free oxygen reacting with methane or as a result of methane oxidation associated with the reduction of sulphates or other compounds (Rad et al. 1996, Carson et al. 2003). Such authigenic carbonates typically precipitate as crusts or concretions at the sediment/seawater interface; they are often divided into high Mg-calcite or low Mg-dolomite groups (Rad et al. 1996, Deyhle et al. 2001).

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METHODS

This study forms part of an integrated research project dealing with petrographic aspects of the Kaczawa mélanges. A standard petrological microscope and a "cold" cathode were used to analyze samples from the boreholes 38/S and 39/S drilled at Stanislawów. Three rock types from the Rzeszówek section (sample *A* – muddy mélange matrix; sample *B* – sandstone olistolith; sample *C* – grey muddy-siliceous slate) and two mélange lithologies from Stanislawów (sample *D* – dark-grey mudstone, borehole 35/S, 24.2-5m; sample *E* – medium-grained green sandstone, borehole 35/S, 915.2-4m) were selected for the investigations. 15 whole-rock X-ray diffraction analyses were carried out. The electron microprobe (EDS & WDS) was used to determine the chemical composition of carbonates from separated heavy mineral fractions (about 100 analytical points). The investigations were performed at the Institute of Geological Sciences at Wroclaw University (XRD Siemens D5005, microprobe /EDS/ Cambridge MK-9, Citl CCL 8200 „cold" cathode, microscope Nikon Eclipse E600-POL) and at the Institute of Geological Sciences - Petrology of the University of Vienna (XRD Phillips, microprobe /EDS, WDS/ CAMECA SX 100).

RESULTS AND DISCUSSION

The XRD analyses showed minor amounts of carbonates to be present in samples *A*, *C* and *E*. Microscope and cathodoluminescence observations revealed the carbonates to be present as: 1) subhedral grains within sandstone layers in dark-grey mudstones of sample *D* and 2) veinlets filling microfractures (e.g. sample 39/S 311,2 m). The carbonates are an important mineral constituent of samples *A*, *C* and *E* types (Kostylew et al. 2003). Qualitative EDS analyses allowed for distinction of two types of carbonates: Ca-Mg-Fe carbonates in the mélange from Stanislawów (sample *E* – 14 vol. %) and Fe-Mg-Mn carbonates in the mélanges from Rzeszówek (sample *A* – 5 vol. % and sample *C* – 81 vol. %). Samples *C* and *E* were chosen for quantitative investigations (Tab. 1).

The carbonates from sample *C* contain 29,95-70,89% of $FeCO_3$, 18,19-62,08% of $MgCO_3$ and 6,72-13,40% of $MnCO_3$. Roughly half of the grains investigated were heterogenous chemically, lighter and darker areas being observed within single grains in BSE images (Tab. 1, Fig. 1). Lighter areas are enriched in siderite whereas darker ones display an intermediary composition between siderite and magnesite. The carbonates from sample *E* may be divided into two groups: 1) grains enriched in siderite which contain only 9,71-11,92% of $CaCO_3$, 18,79-36,64% of $MgCO_3$ and 51,44-70,92% of $FeCO_3$; 2) calcite-rich grains (with a composition close to ankerite) composed of 53,42-57,53% of $CaCO_3$, 12,47-31,66% of $MgCO_3$ and 14,29-31,60% of $FeCO_3$ (Fig. 1). This sample displays also considerable variation of chemical composition within separate grains (Tab. 1, Fig. 1). Darker parts of some grains contain 53,22-64,23% of $CaCO_3$, 30,92-39,25 of $MgCO_3$ and 3,93-9,33% of $FeCO_3$, corresponding with values close to dolomite, whereas two grains are built partly of calcite (~90% of $CaCO_3$, Fig. 1).

Table 1. Selected chemical analyses of carbonates from samples *C* and *E* in wt. %. (Analyses obtained from darker parts of BSE images of the grains are marked grey. Fe was recalculated to Fe^{2+}; Σ of cations = 1).

Sample	***C* - Grey muddy-siliceous slate (Kamiennik/Rzeszówek)**					***E* - Medium-grained green sandstone from Stanisławów (35/S, 915.2-4m)**				
grain no	**2**	**26**		**188**		**17**	**46**		**315**	
SiO_2	0.01	0.01	0.02	0.01	0.02	0.00	0.02	0.07	0.02	1.03
TiO_2	0.01	0.00	0.00	0.02	0.01	0.01	0.00	0.02	0.04	0.01
Al_2O_3	0.02	0.03	0.04	0.14	0.00	0.01	0.03	0.03	0.16	0.75
FeO	41.62	38.23	44.17	39.87	44.36	14.93	7.44	17.08	3.77	11.06
MnO	4.97	5.90	6.23	5.68	5.44	0.94	1.09	1.06	1.78	1.52
MgO	10.71	13.07	6.75	10.74	7.52	11.76	15.38	8.33	14.38	10.35
CaO	0.35	0.13	0.31	0.68	0.15	32.25	35.02	28.58	41.20	31.20
Na_2O	0.02	0.05	0.00	0.08	0.00	0.02	0.00	0.01	0.06	0.10
K_2O	0.01	0.01	0.01	0.01	0.02	0.02	0.00	0.00	0.04	0.15
Total	57.71	57.43	57.52	57.24	57.53	59.94	58.97	55.18	61.44	56.17
Si^{4+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.017
Ti^{4+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Al^{3+}	0.000	0.001	0.001	0.003	0.000	0.000	0.001	0.001	0.003	0.014
Fe^{2+}	0.628	0.563	0.701	0.603	0.698	0.191	0.092	0.245	0.045	0.150
Mn^{2+}	0.076	0.088	0.100	0.087	0.087	0.012	0.014	0.015	0.021	0.021
Mg^{2+}	0.288	0.343	0.191	0.290	0.211	0.268	0.339	0.213	0.304	0.250
Ca^{2+}	0.007	0.002	0.006	0.013	0.003	0.528	0.555	0.525	0.625	0.542
Na^{+}	0.001	0.002	0.000	0.003	0.000	0.001	0.000	0.000	0.002	0.003
K^{+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.003
Σ	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

The results obtained show that the carbonates from the mélanges of the Kaczawa Complex are chemically similar to those of recent accretionary prisms, especially in the case of sample *E* from Stanislawów. The relative enrichment in Fe^{2+} may have resulted from diagenetic and metamorphic processes which affected the Kaczawa Complex deposits. Further investigations of these carbonates may help more closely constrain the hypothesis that the Kaczawa Complex is a fragment of a Variscan accretionary prism.

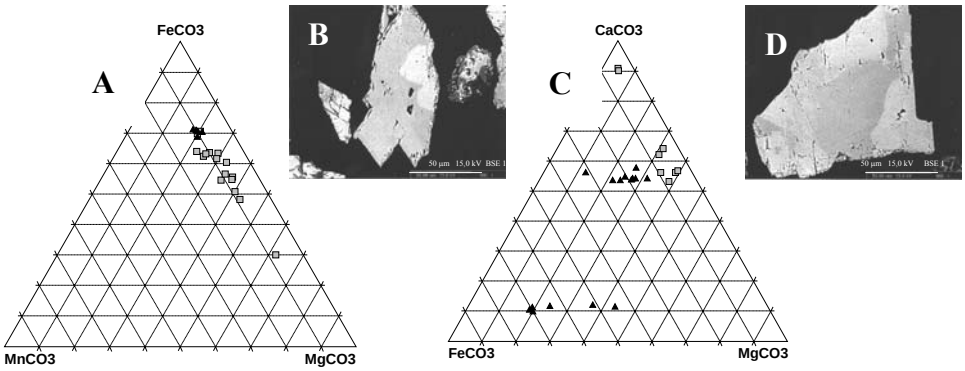

Fig. 1. A & B: Chemical composition and BSE image of carbonates from mélange from Rzeszowek (sample *C*); C & D: chemical composition and BSE image of carbonates from a mélange-type deposit from Stanisławów (sample *E*).
(▲- lighter areas of grain; □ - darker areas of grain)

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