Application of X-Ray diffraction analysis for sedimentological investigation of Middle Devonian dolomites from Northeastern Bulgaria

Polina Andreeva¹, Ventsislav Stoilov², Ognyan Petrov²

¹Geological Institute, Bulgarian Academy of Sciences, Sofia 1113, Acad. G. Bonchev St., Block 24, Sofia 1113, Bulgaria
e-mail: polina_a@geology.bas.bg
²Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 107, Sofia 1113, Bulgaria
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Abstract. The studied Middle Devonian (Givetian) dolomites occur in three well sections: OP-2 Mihalich, R-119 Kardam and R-1 Vaklino (Northeastern Bulgaria). Two general genetic dolomite groups are distinguished and interpreted on the basis of performed XRD analyses and petrographic observations. The first one is represented by early diagenetic crypto- to microcrystalline dolostones that are characterized by nearly stoichiometric composition (from 51.0 to 51.7 mole % CaCO₃) and degree of order ranging from 0.50 to 0.91. They are interpreted as products of rapid precipitation in an arid peritidal (sabkha) environment with hypersalinity of the water milieu and elevated Mg/Ca ratio of the dolomitizing solutions. The second group includes late diagenetic medium crystalline dolostones that have almost stoichiometric composition (from 50.0 to 51.3 mole % CaCO₃) and higher degree of order (from 0.77 to 1.18) indicating a possible slow crystallization process and precipitation from dilute solutions at elevated temperatures in an open diagenetic system. A part of them might have also resulted from neomorphic alteration of precursor metastable dolomite phases.

INTRODUCTION

Dolomite includes a group of minerals with similar but not identical Mg/Ca ratios and a range of chemical variations and lattice structures (Warren, 2000). It comprises an array of natural Ca-Mg carbonates with chemical compositions close to ideal dolomite, but with weak or diffuse X-ray diffraction (XRD) reflections that indicate varying degree of cation disorder (Hardie, 1987). Thus, the XRD method has been widely used in analyzing stoichiometry and degree of order of the dolomite crystal lattice. Generally, natural dolomites in sedimentary rocks are nonstoichiometric (CaₓMg₁₋ₓCO₃) and show an excess of Ca²⁺ up to Ca₂MgCO₃ or less commonly Mg²⁺ up to Ca₉Mg₂CO₃ (Tucker and Wright, 1990). The dolomite stoichiometry can be determined by measuring the displacement of the (104) peak relative to a standard. This is the effect of increasing d lattice spacing because of calcium substitution for magnesium cations (Goldsmith and Graf, 1958). The sharpness and relative intensities of a set of superstructural peaks (021), (015) and (101) are also used for measuring the degree of ordering of the dolomite crystal lattice. Although the dolomitization is one of the most studied diagenetic processes in carbonate sedimentology, the factors that control the composition and cation order of the resultant dolomite remain poorly understood (Dawans and Swart, 1988; Kaczmarek and Sibley, 2011).

In this paper we investigate Middle Devonian (Givetian) dolomite-bearing sediments in three well sections (OP-2 Mihalich, R-119 Kardam and R-1 Vaklino) from Northeastern Bulgaria (Fig. 1). The aims of the study are to determine the dolomite stoichiometry and ordering by XRD analysis and to use the obtained results together with petrographical data for genetic interpretation of the different early and late dolomite phases.

Stratigraphy

Devonian sediments from Northeastern Bulgaria are established only in deep wells where the dolostones commonly occur in Givetian successions of the carbonate-
sulphate formation, dolomite formation, and banded limestone formation (Yanev, 1972; Yanev and Boncheva, 1995, Fig. 2). The Middle Devonian age of these rocks was proved by means of conodonts by Spassov (1987), Boncheva (1995) and Boncheva et al. (2000).

The Givetian sediments of the carbonate-sulphate formation in R-119 Kardam (1432–2800 m) and R-1 Vaklino (2051–3179 m) wells are represented by sulphate rocks (anhydrites), dolostones (dolomudstones, dolomitic microbial bindstones), limestones (bioclastic mud-
stones, wackestones and packstones, peloidal grainstones, lithoclastic floatstones/rudstones) and rare black shales. In OP-2 Mihalich this unit is correlated with a limestone-dolostone package (1409–2372 m) (Lakova and Yanev, 1989) which is composed of limestones (mudstones, bioclastic wackestones and floatstones, peloidal packstones and microbial bindstones) and crystalline dolostones. The dolomite formation occurs in all studied wells – OP-2 Mihalich (1381–1409 m), R-119 Kardam (1053–1432 m), R-1 Vaklino (1970–2051 m) consisting of crystalline dolostones and subordinately presented limestones (bioclastic and homogeneous mudstones, intraclastic floatstones/rudstones and microbial bindstones). The banded limestone formation in OP-2 Mihalich (1381–1086 m), R-119 Kardam (924–1053 m) and R-1 Vaklino (1835–1970 m) wells is built of predominant limestones (bioclastic floatstones, peloidal packstones/ grainstones and microbial bindstones) and rare crystalline dolostones.

**Depositional setting**

The Givetian sediments of the described units are interpreted as a typical peritidal succession which is represented by clearly distinguished shallow subtidal bioclastic limestones, intertidal microbial mats plus intraformational breccias, and supratidal carbonates and evaporites (Andreeva, 2007; Andreeva et al., 2010). According to this interpretation in Givetian time the deposition took place in an arid low-energy tidal-flat setting with restricted or semi-restricted water circulation and locally developed supratidal sabkha evaporites (anhydrite rocks from the carbonate-sulphate formation). The observed alternation of subtidal, intertidal and supratidal successions in the sections suggests a cyclic character of the Givetian sedimentation. The tidal-flat deposition continued later during the Givetian (dolomite formation and banded limestone formation) but without discrete evaporite precipitation.

**METHODOLOGY**

The studied dolomites occur in three well sections (OP-2 Michalich, R-119 Kardam and R-1 Vaklino) and are established in several informal lithostratigraphic units: carbonate-sulphate formation, dolomite formation and banded limestone formation. Sixty thin sections of rock-forming dolomite were examined under standard petrographic microscope. The most representative of them were stained with Alizarin Red S and potassium ferricyanide (Dickson, 1966) and a reduced number of fourteen dolomite samples (which did not contain more than 1% FeO – see Sperber et al., 1984) were selected for XRD analyses. Almost all samples are from homogeneous dolomites because heterogeneous dolostones exhibit multiple peaks and/or shoulders (cf. Jones et al., 2001). Broken dolostone surfaces were studied by means of JEOL Superprobe 733 scanning electron microscope to obtain more detailed textural information.

The XRD analyses were carried out using powdered bulk rock material and were performed on a DRON 3M powder X-ray diffractometer (Institute of Mineralogy and Crystallography “Acad. Ivan Kostov”, BAS) using Fefiltered CoKα radiation. The samples were step-scanned in the 10–65° 2θ interval. In part of them (without quartz and/or anhydrite content) metal silicon was used as internal standard. The d-spacing of the dolomite peak (104) and the relative intensities of the (015) and (110) peaks (computed as integral intensities) were measured on the XRD patterns. The excesses calcium was calculated using the equation of Lumsden (1979): mole % CaCO3 = Md + B, where M = 333.33, and B = −911.99, observing the required condition that the samples should not contain more than 20% quartz. Additionally, the degree of order of the dolomite crystal lattice was estimated as a ratio between the intensities of the (015) and (110) peaks (Füchtbauer and Goldschmidt, 1965).

**RESULTS**

**Dolostone petrography and distribution**

In the present work, two petrographic dolostone varieties were analyzed: 1) crypto- to microcrystalline dolostones; and 2) medium crystalline dolostones. The classification scheme of Sibley and Gregg (1987) was applied to describe various dolomite rock textures.

**Crypto- to microcrystalline dolostones**

These dolostones occur only in the carbonate-sulphate formation from R-119 Kardam and R-1 Vaklino well sections where they have mimetically replaced primary intertidal/supratidal sediments and are closely associated with evaporites (anhydrites). They are represented by dolomudstones and dolomitic microbial bindstones with well preserved fabrics being composed of dolomite crystals having size from <4 µm to 15 µm (Figs 3 a-c). The dolomudstones consist of homogeneous dolomitic matrix that locally contains scattered needle-like anhydrite crystals (Fig. 3a) or sporadic thin-shelled ostracods. According to Sibley and Gregg’s (1987) classification these dolomites are defined as unimodal or polymodal planar-s and planar-e dolomitic micrites with completely mimetically replaced matrix. On the other hand, the investigated microbial bindstones (Fig. 3b) consist of dolomicritic/dolomicrosparitic laminae with homogeneous or clotted fabric and commonly represented peloid grains. Rare oval or irregular in shape fenestrae are also observed. These dolostones can be classified as unimodal or polymodal planar-s and planar-e mimetically replaced dolomitic microbial bindstones.

**Medium crystalline dolostones**

These dolostones are established in all studied well sections in the carbonate-sulphate formation (limestone-dolostone package), dolomite formation and banded limestone formation. Most of them are pure monomineral rocks but calcareous dolostones also occur sporadically. The dolostones are characterized by crystalline mosaics (Figs 3d-f) represented predominantly by medium crys-
Fig. 3.

a – Polymodal planar-e dolomitic micrite with completely mimetically replaced matrix containing scattered needle-like anhydrite crystals (white arrow). R-119 Kardam, carbonate-sulphate formation, NII;
b – Polymodal planar-s mimetically replaced dolomitic microbial bindstones. R-119 Kardam, carbonate-sulphate formation, NII;
c – SEM view of polymodal planar-s dolomicrite with anhydrite crystals (white arrow). R-119 Kardam, carbonate-sulphate formation;
d – SEM view of polymodal planar-s medium crystalline dolomite. R-119 Kardam, dolomite formation;
e – Polymodal planar-s medium crystalline dolomite. The dolomite crystals commonly display cloudy cores and clear rims. R-1 Vaklino, dolomite formation, NII;
f – Polymodal planar-s bioclastic dolomite with completely replaced groundmass and partly replaced allochems. Scarce poorly preserved crinoid ossicles (white arrow) are locally observed. OP-Mihalich, limestone-dolostone package of carbonate-sulphate formation, stained thin section, NII.
talline dolomite crystals (62–250 µm). However, in some thin-sections both fine- (<62 µm) and medium-sized dolomite crystals are observed. The latter commonly display cloudy cores and clear rims (Fig. 3e). Scarce poorly preserved fossil remains (mostly crinoid ossicles and brachiopod shells) likewise occur in the more calcareous varieties (Fig. 3f). The pure dolostones are defined as unimodal or polymodal non-planar or planar-s dolostones, and the calcareous dolostones are defined as polymodal planar-s bioclastic dolostones with completely replaced groundmass and partly replaced allochons.

**XRD analyses of the dolostones**

The obtained results from the performed XRD analyses show that crypto- to microcrystalline dolomudstones (dolomudstones and dolomitic microbial bindstones) have nearly stoichiometric composition and very close values – from 51.0 to 51.7 mole % CaCO$_3$. They are characterized by degree of order ranging from 0.50 to 0.91 (Fig. 4). The samples from medium crystalline dolostones have almost stoichiometric composition (from 50.0 to 51.3 mole % CaCO$_3$) and higher degree of order (from 0.77 to 1.18, Fig. 4). It should be mentioned that the finely to medium crystalline dolostone varieties display lower ordering values (0.77 and 0.84) than the medium crystalline dolostones (from 1.04 to 1.26) (Fig. 4).

**DISCUSSION**

In this paper the Devonian dolostones are compared and referred to different genetic dolomite groups distinguished by Lumsden and Chimahusky (1980) and Morrow (1982). Based on stoichiometry, texture and presence/absence of associated evaporites these authors identified three main groups of dolomites: 1) coarse-crystalline near-stoichiometric (50.0–51.0 mole % CaCO$_3$) dolomites, 2) finely crystalline Ca-rich (54.0–56.0 mole % CaCO$_3$) dolomites, not associated with evaporites, and 3) finely crystalline nearly stoichiometric (51.0–52.0 mole % CaCO$_3$) dolomites associated with evaporites. Group 1 dolomites are generally of late diagenetic burial origin, whereas the second and third groups are usually near-surface early diagenetic.

The studied crypto- to microcrystalline dolostones (dolomudstones and dolomitic microbial bindstones) closely associate with sulphate rocks (anhydrites) and are characterized by nearly stoichiometric composition (51.0–51.7 mole % CaCO$_3$, Fig. 4). Thus, they can be referred to the early diagenetic third group of “finely crystalline nearly stoichiometric dolomites associated with evaporites” (Lumsden and Chimahusky, 1980; Morrow, 1982). The limited presence of crypto- to microcrystalline dolomites only in the intertidal/supratidal facies (Andreeva, 2007) together with nodular and
enterolithic sabkha anhydrites likewise testifies to their early diagenetic penecontemporaneous peritidal origin. The observed facies association and diagnostic dolomite crystal size features suggest that these dolomircites were probably formed by an evaporitic (sabkha) or seepage-reflux model. Similar very fine grained non-fossiliferous dolostones commonly occur in modern and ancient evaporitic tidal flat settings (Illing et al., 1965; Tucker and Wright, 1990) where numerous nucleation sites in the replaced aragonite mud result in formation of micron-sized dolomite crystals and good textural preservation.

Generally, it is assumed that the degree of enrichment of Ca in dolomites reflects the Mg/Ca ratio of the fluids from which they are formed (Füchtbauer and Goldschmidt, 1965; Morrow, 1978; Lumsden and Chimahusky, 1980). The strong relationship between fluid chemistry and dolomite composition has also been proved recently by Kaczmarek and Sibley (2011) in a series of high-temperature dolomitization experiments. These authors concluded that the rate of dolomitization and dolomite composition is a function of the initial solution, where higher Mg/Ca ratios lead to rapid dolomitization rates and more stoichiometric dolomite. On the other hand, a relation between near-stoichiometric dolomite composition and arid (evaporitic) conditions has also been documented (Goldsmith and Graf, 1958; Füchtbauer and Goldschmidt, 1965; Füchtbauer, 1972, 1974). The occurrence of predominantly nearly stoichiometric dolomites in modern arid settings and prevalent Ca-rich dolomites in humid areas (Deffeyes et al., 1965; Illing et al., 1965; Shinn et al., 1965; Füchtbauer, 1974; Morrow, 1982) likewise support this supposition. Following all these suggestions, it could be presumed that the nearly stoichiometric composition of the investigated crypto- to microcrystalline dolostones indicates rapid dolomitization rates and precipitation of Mg-rich fluids. Most probably their formation was related to the existence of an arid peritidal (sabkha) environment during the Givetian in the present territory of Northeastern Bulgaria (Andreeva, 2007; Andreeva et al., 2010) with hypersalinity of the water milieu and elevated Mg/Ca ratio of the dolomitizing solutions due to precipitation of sulphate minerals (gypsum and anhydrite). Similar penecontemporaneous dolomite formation, promoted by elevated salinity and increased Mg/Ca, has been documented in some recent evaporitic peritidal settings (Deffeyes et al., 1965; Kinsman, 1966; Land 1967). According to Morrow (1982) such early diagenetic stoichiometric finely crystalline dolomites originate from pore fluids with Mg/Ca ratio from >6:1 to 22:1 and salinity exceeding 35‰.

It is widely accepted that dolomites that are non-stoichiometric are less well ordered, which is also proved in the present study. Thus, the crypto- to microcrystalline dolostones are less stoichiometric and display lower degree of order in comparison with more stoichiometric and better ordered medium crystalline dolostones (Fig.4). A similar trend, comparing the degree of order and stoichiometric composition of ancient peritidal dolomrites and late diagenetic pervasive dolomites, was also documented by other authors (Hird, 1986; Chatalov and Stanimirova, 2001). Generally, recent dolomites are also less ordered and metastable compared to ancient ones, i.e. there is a progressive stabilization developed during the dolomite diagenesis. However, the investigation of Wenk et al. (1983) has proved the coexistence of both ordered and less ordered dolomites in the modern coastal Abu Dhabi sabkha which is a result of changing temperature and fluid chemistry in response to environmental parameters. This investigation also demonstrates that the ordered dolomites are generally not formed by ordering of a disordered dolomite but result from direct precipitation. According to these conclusions and considering the early diagenetic penecontemporaneous peritidal origin of the studied cryptro- to microcrystalline dolostones it could be suggested that the degree of ordering of these dolomites is an effect from direct precipitation in an evaporite depositional environment.

The medium crystalline dolostones are distinguished by almost stoichiometric composition (50.0–51.3 mole% CaCO$_3$, Fig. 4) and can be related to the late diagenetic “coarsely crystalline near-stoichiometric dolomite group” (Lumsden and Chimahusky, 1980; Morrow, 1982). These dolostones occur in different lithostratigraphic units (limestone-dolostone package of the carbonate-sulphate formation, dolomite formation and banded limestone formation) and do not show any relation to depositional facies. The observed cloudy cores and clear rims in the dolomite crystals (Fig. 3e) are common features in many late diagenetic dolostones and testify that precipitation did not take place in one event (e.g. penecontemporaneous early diagenetic dolomrites) but over a much longer period of time from shallow into deeper burial (Tucker and Wright, 1990). Thus, it could be assumed that the nearly stoichiometric composition of the studied medium crystalline dolostones and their higher degree of order in comparison to the crypto- to microcrystalline dolostones (Fig. 4) most probably indicate a slow crystallization process and precipitation from dilute solutions and at elevated temperatures in an open diagenetic system (Sperber et al., 1984; Morrow, 1978; 1982). According to Morrow (1978, 1982) continued slow crystal growth may overshadow the influence of low fluid Mg/Ca ratios and cause the formation of nearly stoichiometric dolomites with good crystal ordering. However, a part of these late diagenetic dolostones might also be a result from dolomite neomorphism of precursor metastable dolomite phases (cf. Sperber et al., 1984, Land 1985; Gregg et al., 1992). On the other hand, the observed finer crystal size and lower degree of order of the finely to medium crystalline dolomite varieties (in comparison with the dolostones composed only of medium-sized dolomite crystals) (Fig. 4) might reflect lower stabilization rates. Although the obtained petrographic and XRD data proved the late diagenetic origin of the medium crystalline dolomites additional geochemical study of dolomite is required for more precise interpretation of the dolomitization model.

**CONCLUSIONS**

In this study dolomite stoichiometry and ordering degree were determined by means of XRD analysis and were combined with petrographical data for genetic interpretation of the investigated Givetian dolostones. Thus, the
Intracellularly and extracellularly, Mg–Ca carbonate minerals are often involved in a variety of biological processes, including plant cell walls, calcified structures in marine organisms, and the biomineralization of skeletons in invertebrates. The Mg/Ca ratio influences the crystal structure and stability of these minerals, which in turn affects their physical and chemical properties. This study was accomplished at the Geological Institute and the Institute of Mineralogy and Crystallography (Bulgarian Academy of Sciences). Part of it is a contribution to a Student Research Grant, financed by the SE Europe Geoscience Fondation.

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