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Mineral chemistry of gersdorffite – A powerful tool in the differentiation of hydrothermal systems

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ABSTRACT

Gersdorffite from two mineralization types (post-Variscan vein deposits, strata-bound mineralization) was investigated in the Niederberg area Rhenish Massif. In the ternary Ni–Co–Fe space gersdorffite from post-Variscan vein deposits displays a tight cluster with the highest Ni-contents ranging from 0.825 to 0.962 atoms per formula unit (a.p.f.u.). As/S ratios comprise a narrow range from 0.875 to 1.012. In contrast gersdorffite from the strata-bound mineralization displays a substitutional trend. Co and Fe substitute for Ni in a $\pm$ fixed ratio. Ni ranges between 0.494 and 0.836 a.p.f.u. As/S ratios (1.025–1.211) display a wider range and indicate higher As-contents relative to gersdorffite from post-Variscan vein deposits. Based on these results, two different hydrothermal fluid systems can be identified in the Niederberg area forming gersdorffite in both mineralization types. The hydrothermal fluids circulating in the post-Variscan vein deposits were homogeneous (high Ni-activities, lower As fugacities) and mixing occurred far away from the site of deposition whereas the fluids of the strata-bound mineralization were more heterogeneous (decreasing Ni-activities) with moderate elevated As fugacities. With respect to the post-Variscan vein deposits in the Niederberg area the results are compatible with earlier findings.

Comparison with available gersdorffite analyses from adjacent areas (borehole Viersen, Ramsbeck deposit) reveal that gersdorffite compositions provide a reliable tool in distinguishing between different hydrothermal systems on a regional scale in the northern Rhenish Massif. However, gersdorffite compositions cannot be used to discriminate between Variscan and post-Variscan deposits with confidence.

The country rocks in the Niederberg area are possible sources for Ni, Co and Fe during gersdorffite formation of the strata-bound mineralization. However, due to the remarkable homogeneity of gersdorffite compositions of the post-Variscan vein deposits irrespective of age and composition of the immediate adjacent host-rocks it is assumed that these host-rocks are not the source of the metals. Reduced Zechstein sulfate is assumed to be the source of sulfur. The As source remains unknown.

Due to conflicting experimental data concerning the gersdorffite solid solution field it is not possible to derive reliable formation temperatures for the strata-bound mineralization. However, gersdorffite compositions of the post-Variscan vein deposits are compatible with low formation temperatures (<300 °C) in accordance with earlier findings.

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1. Introduction

Gersdorffite (NiAsS) occurs in hydrothermal vein deposits at moderate temperatures (Anthony et al., 1990) but also in magmatic sulfide systems (Marshall et al., 2004). The former authors list numerous occurrences worldwide.

Gersdorffite accommodates Ni, Co and Fe in varying proportions thus forming solid solutions in the ternary gersdorffite–cobaltite–arsenopyrite series. Moreover, the As and S content can deviate from the molar 1:1 ratio thus forming solid solutions towards krutovite ($NiAs_2$) and vaesite (NiS_2). This should provide a tool in distinguishing gersdorffite from different hydrothermal systems. The major objectives of this investigation are (i) quantitative description of the mineral chemistry of gersdorffite from the Niederberg area. (ii) Identifying hydrothermal fluid systems based on different gersdorffite compositions from the Niederberg area and comparison with analyses from adjacent areas. Furthermore the possible element sources are discussed. (iii) An attempt to estimate formation temperatures comparing gersdorffite compositions with experimentally determined gersdorffite solid solution fields.

In the Niederberg area, gersdorffite bearing samples were recovered from post-Variscan vein deposits (numbers according to Fig. 1): 1=Neu-Diepenbrock Mine III, Mülheim/Ruhr (Gauss Krüger grid: R ^{25}60250 H ^{56}93750, topographic map 4607, Heiligenhaus sheet); 2=trials near shaft Ernst, Lintorf

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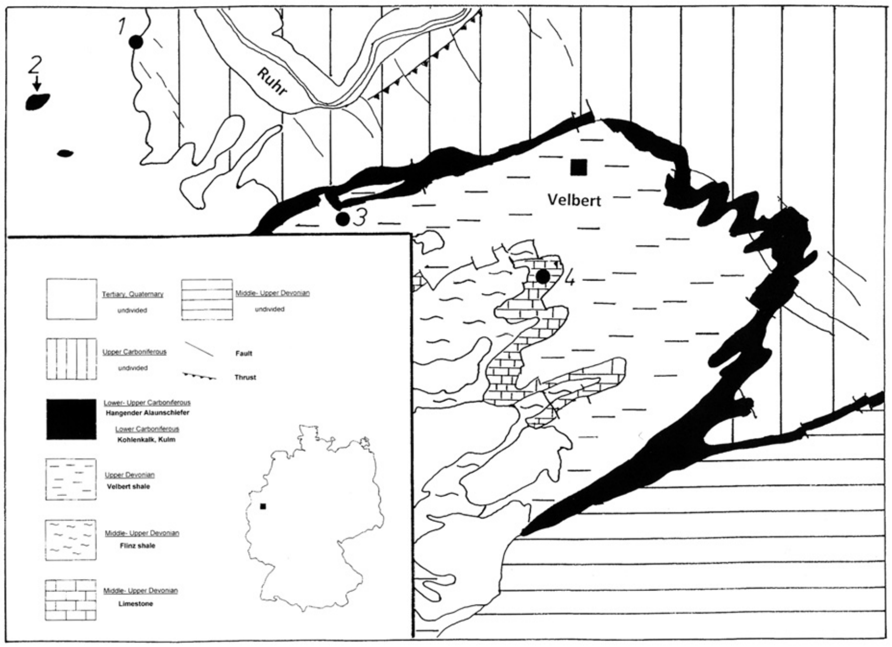

Fig. 1. Simplified geological map of the Niederberg area. Drawing based on the geological map C 4706 Düsseldorf-Essen (1980, Geologischer Dienst, Krefeld). Post-Variscan vein deposits: 1 = Neu-Diepenbrock III Mine, Mülheim/Ruhr; 2 = Trials near shaft Ernst, Lintorf; 3 = Thalburg Mine, shaft Luis, Heiligenhaus. Strata-bound mineralization: 4 = Rohdenhaus quarry, Wülfrath. The distance between sampling sites 1 and 3 is ca. 8 km.

(Gauss-Krüger grid: R ^{25}57750 H ^{56}92038, topographic map 4606, Düsseldorf-Kaiserswerth sheet); 3 = Thalburg Mine, shaft Luis, Heiligenhaus (Gauss-Krüger grid: R ^{25}66675 H ^{56}88625, junction Talburgstraße-Schopshofer Weg, topographic map 4607, Heiligenhaus sheet). A strata-bound gersdorffite bearing mineralization was discovered in the Rhodenhaus quarry (4 in Fig. 1; limestone), Wülfrath (Gauss-Krüger grid R ^{25}72000 H ^{56}87000, topographic map 4608, Velbert sheet). The position of the sampling sites is illustrated in Fig. 1.

2. Geological description

The Niederberg area between the rivers Ruhr in the north and Wupper in the south is part of the northwestern margin of the Rhenish Massif east of the Rhine valley. The Rhenish Massif forms a fold-and-thrust belt and is part of the northern external zone (Rhenohercynian) of the Central European Variscan orogen. It is composed of marine Lower Devonian to Upper Carboniferous volcano-sedimentary rocks (siliciclastic sediments of pelitic to psammitic compositions, carbonates, black shales plus acidic and basic volcaniclastic rocks) which were deposited in the Rhenohercynian basin. In the early Upper Devonian south directed subduction due to the activation of the continental margin of the Mid-German Crystalline Rise started with accretion of shelf sediments during the early Carboniferous (Francke and Oncken, 1990). During this process the rock sequences in the Rhenohercynian basin were deformed, resulting in a NE–SW strike of fold axes, S_1 foliation and the major thrust systems (Oncken, 1984, 1988). The deformation started in the south and the deformational wave progressed to the north. According to Ahrendt et al. (1983), peak metamorphic ages range in the south from 327–318 to 305–290 Ma at the northern margin of the Rhenohercynian. In general, Oncken (1991) and Dittmar et al. (1994) found very low grade metamorphic conditions, with peak metamorphic temperatures in the range of 180–320 °C.

The Niederberg area is composed of marine siliciclastic and biogenic sedimentary rocks (Middle Devonian to Upper Carboniferous). Fig. 1 displays a simplified geological overview. North of the Niederberg area Upper Carboniferous shales, greywackes and sandstones of the Ruhr area intercalated with huge coal seams crop out or are lying in the subcrop beneath Cretaceous, Tertiary and Quaternary sediments further to the north. Towards the west the Paleozoic strata of the Niederberg area are increasingly covered by Tertiary and Quaternary sediments of the Lower Rhine Embayment. In the northwestern part of the Niederberg area at Lintorf two minor anticlines made up of Lower Carboniferous rocks (Hangender Alaunschiefer, Kohlenkalk) emerge between Tertiary and Quaternary sediments. Beside Middle to Upper Devonian limestones (Givet – Adorf), Velbert shales (shales intercalated with silt- and sandstones, Upper Devonian), Flinz shales (shales with intercalated sandstones, Middle–Upper Devonian) and Middle Devonian conglomerates (for clarity not shown in Fig. 1) constitute the core of the northeast plunging Velbert anticline, the dominant tectonic structure in the Niederberg area (Fig. 1). The main strike direction of the fold axes in the Niederberg area is NE–SW. The limbs of the Velbert anticline are composed of Lower Carboniferous, partly dolomitized, limestones (Kohlenkalk) which grade laterally along the southeastern limb of the Velbert anticline into the anoxic Kulm strata (black and siliceous shales, Lower Carboniferous) indicating a progressively deeper basin sedimentation. Both, Kohlenkalk and Kulm strata are conformably overlain by the “Hangender Alaunschiefer” (pyritiferous black shales). In these black shales the stratigraphic change between Lower and Upper Carboniferous is established. The metamorphic grade of the sedimentary rocks in the Niederberg area is very low but increases within the Velbert anticline, according to chlorite geothermometry, from northeast to southwest (Harms, 2001). A comprehensive geologic overview of the Niederberg area is given by Richter (1996).

Numerous NNW–SSE trending ore veins of post-Variscan origin are distributed in all rock types throughout the Niederberg area. The ore veins were mined from the Middle Ages until 1916. Galena, sphalerite and chalcopyrite are the dominant sulfide

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