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The first record of siegenite $(Ni,Co)_3S_4$ from the Netherlands

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Abstract

Epigenetic mineralisations occurring in the former coal-mining district of Limburg predominantly consist of sphalerite, galena, chalcopyrite, quartz, Fe-dolomite/ankerite and calcite. The present note describes siegenite which was collected for the first time from this paragenesis some years ago.

Keywords: hydrothermal mineralizations, Limburg, siegenite, Carboniferous

Introduction

When collieries in southern Limburg (the Netherlands) were still in operation, epigenetic mineralisations were encountered in sediments of Westphalian (Late Carboniferous) age, and records of such date back to the earliest days of mining (Leggewie & Jongmans, 1931). The first detailed descriptions may be found in Douw & Oorthuis (1945) and in De Wijkerslooth (1949).

From the area bordering the province of Limburg in the southeast, epigenetic mineralisations have long been known. The extensive ore bodies were of economic use, which led to mining activities around La Calamine, Schmalgraf and Fossey (Belgium) and in the vicinity of Aachen and Stolberg (Diepenlinchen and Breinigerberg, Germany). Based on numerous exposures and a number of boreholes, it has been determined that the Palaeozoic basement of and around the Lower Rhine Embayment contained varying amounts of such deposits everywhere (Clausen & Stadler, 1998). The provenance and mechanism of mobilisation and deposition of hydrothermal solutions was discussed by Krahn et al. (1986), to which reference is made.

The mineralisations occurring in the Limburg Westphalian predominantly consist of sphalerite, galena, chalcopyrite, quartz, Fe-dolomite/ankerite and calcite. Less common are pyrite and marcasite while barites is extremely rare. These mineralisations occurred almost exclusively in sandstones and quartzitic sandstones (NITG-TNO, 1999). In addition, dickite is common, mainly in pseudobreccias of sandstones and sandy shales, formed by hydrothermal erosion. Mineralisations occurring in the Limburg Westphalian are comparable to those of the coal measures of Aachen, Erkelenz and the Ruhr area (Buschendorf et al., 1957; Stolze, 1961), and are related to surfaces of numerous, mostly SE-NW trending faults. Particularly in those places where these cut the flanks of the Waubach Anticline, important concentrations of the above-mentioned mineralisations have been encountered (see map IV in Kimpe et al., 1978). In this species-poor paragenesis, siegenite has recently been documented, which is here described.

Co-Ni-sulphides in the Palaeozoic of Limburg and environs

In his studies of epigenetic mineralisations, De Wijkerslooth (1949) was the first to report the presence of bravoite, stannite and linnaeite. Some authors (Grondijs & Schouten (in Douw & Oorthuis, 1945), Douw & Oorthuis 1945, Kimpem 1980) have expressed doubts about these identifications. The only other Ni-Co-sulphide on record is millerite, a highly typical Ni-sulphide, occurring sporadically in a characteristic, needle-shaped habit. From the Dinantian (Lower Carboniferous) of borehole Thermae 2000 (Valkenburg aan de Geul, the Netherlands), Friedrich et al. (1987) recorded a Pb-Zn mineralisation with bravoite crystals in 'schalenblende'. Other records of Co-Ni-sulphides and -arsenides in the direct vicinity of from the Limburg coal measures are those by Krahn et al. (1986), concerning bravoite, vaesite and cattierite from the Aachen-Stolberg area, and by Redecke et al. (1998), concerning bravoite, vaesite and (Fe-Co-) gersdorffite with transitions to Ni-rich arsenopyrite, from various wells in the Lower Rhine Embayment. Within the mineralisations that are genetically linked to tectonic structures in the Ruhr area, there are a handful of records of linnaeite from the collieries Christian Levin (Essen-Dellwig) (Buschendorf et al., 1957), Vereinigte Hannibal (Bochum) (Hesemann et al., 1961) and Westende (Duisburg-Laar) (Pilger, 1961).

Material and methods

The siegenite was encountered on the waste dump of the former state collieries Emma and Hendrik at Brunssum, where from 1996 onwards, various finds have been made. For laboratory analyses, the siegenite crystals collected in 1996 were used - these are now deposited in the collections of the Natuurhistorisch Museum Maastricht (NHMM, registration numbers 2001 090-092). All other material available is housed in the author's collections (registration nos 1565, 1918, 1948, 2014 and 2213). The exact geographic and stratigraphic provenance of the siegenite can no longer be determined. The concession areas roughly extended between Geleen and Hoensbroek and the Upper Carboniferous strata exposed at both collieries comprised almost exclusively Westphalian A and B.

Results and discussion

As noted above, the occurrence of epigenetic mineralisations is almost exclusively linked to sandstone. In addition, small quantities occur in cavities in 'clay siderite' concretions with a septarian structure. These concretions are very common especially in *Stigmaria*-bearing 'seat earth'; they were described in detail by Kimpe (1956). All siegenite collected comes from these sandstones and concretions, and consists of idiomorph crystals and crystal aggregates.

Tab. 1. XRD data of siegenite from the Westphalian of Dutch Limburg, in comparison with PDF-2 sheet 43-1477 (natural siegenite).

Brunssum siegenite		**PDF-2 43-1477**			
2θ	I/I	2θ	I/I	d	hkl
16.31	18	16.287	19	5.438	1 1 1
26.75	33	26.742	32	3.331	2 2 0
31.47	100	31.475	100	2.840	3 1 1
32.90	3	32.915	3	2.719	2 2 2
38.17	83	38.193	67	2.3545	4 0 0
47.23	7	47.244	8	1.9224	4 2 2
50.29	46	50.303	37	1.8124	5 1 1
55.08	91	55.126	58	1.6647	4 4 0
64.84	6	64.876	5	1.4361	5 3 3
69.00	6	69.039	6	1.3593	4 4 4
77.83	9	77.843	7	1.2261	7 3 1

The (powder-) XRD compares well with chart 43-1477 (natural siegenite) of the ICDD PDF-2 data base. Strong reflections have been noted, of d = 5,43 (18); 3,33 (33); 2,84 (100); 2,35 (83); 1,81 (46) and 1,66 (91). A few peaks (the most intensive one at 2θ 37,08) may be explained by the occurrence of pyrite. Most crystals are scattered over Fe-dolomite/ankerite rhombs, while some have formed on chalcopyrite crystals. In two specimens, siegenite and millerite co-occur. The size of the siegenite crystals varies between 0.5 and 1.0 mm. SEM analyses have clearly shown the crystals to consist of a combination of a predominant octahedron and diminutive hexahedral faces (Fig. 1). The crystals are bright grey in colour, some showing the characteristic purplish hue, and display a clear metallic luster.

The chemistry of the linnaeite group was studied by Vokes (1967), on the basis of material from the Upper Precambrian Raipas Group (Raipas and Borras formations) of Norway. In addition, Vokes re-analysed previously described samples by Tarr (1935). There is a high degree of substitution of Fe, Ni, Co and Cu in the structure, with siegenite defined within the linnaeite group by a Ni/Co ratio of 1:1, and thus positioned between polydymite and linnaeite. Native samples usually have a slightly higher Ni-value and small amounts of Fe and Cu, which holds also true for the specimens described in the present paper. EDX analyses have shown the Ni/Co ratio in NHMM

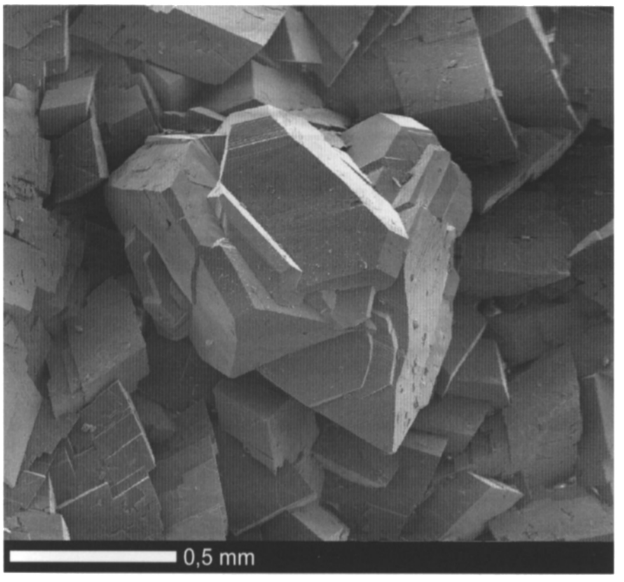

Fig. 1. Siegenite on Fe-dolomite/ankerite, collections of the Natuurhistorisch Museum Maastricht (NHMM 2001 090).

2001 092 to be almost in equilibrium, whereas NHMM 2001 090 and NHMM 2001 091 show amounts of Ni and Co of 45.27 and 33.05 weight %, respectively. Cu has not been demonstrated, while the Fe-content is about 2.5 weight %

De Wijkerslooth's (1949) record of linnaeite in the Limburg Westphalian is based on a single occurrence in the state mine Domaniale at Kerkrade. However, subsequent authors have expressed strong doubts over his interpretation. On the basis of the material at hand now it is clear that the Co-Ni linnaeite-member siegenite does occur in the Upper Carboniferous of Dutch Limburg. It has not yet been determined whether it forms part of the hydrothermal mineralisation or if its genesis is related to an earlier sulphidic phase in which Co and Ni acted as sources. In addition, the mineral occurrences of the Limburg coal measures have been extensively sampled in the past, which has resulted in a large and well-documented collection, currently housed at the Nationaal Natuurhistorisch Museum (Naturalis, Leiden). Of this collection, so far only a small portion has been studied and described. It is quite possible that it will yield more information concerning siegenite distribution and position in the paragenetic sequence.

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