

# Impact-induced carbonate-psilomelane vein in the Azuara structure of northeastern Spain

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The southwestern rim area of the Azuara impact structure in northeastern Spain [1, 2, 3, 4] is characterized by a variety of quite different impact breccia dikes. Close to the village of Monforte de Moyuela, an outcrop was found where autochthonous Muschelkalk dolomite is crosscut by a dark vein (UTM coordinates of the outcrop are 06 67 200/ 45 46 300). The width of the vein is about 5 cm.

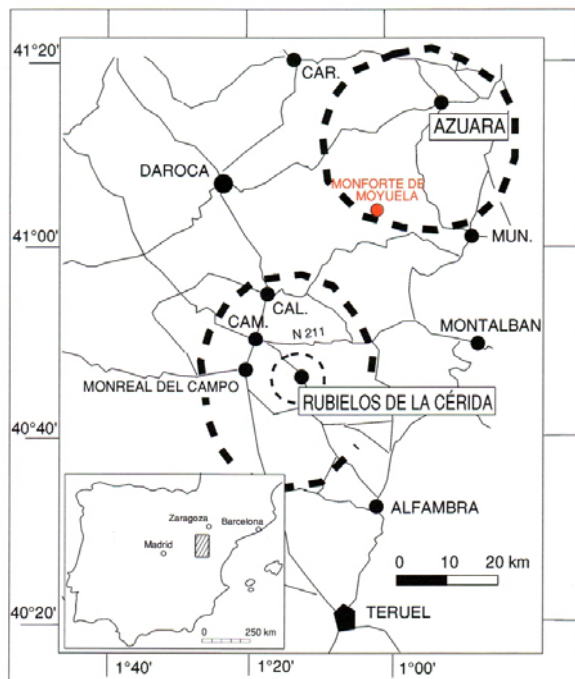


Fig. 1: Azuara impact structure located south of Zaragoza and north of the companion Rubielos de la Cérda impact structure [5, 6, 7]



Fig. 2: Outcrop of Muschelkalk dolomite crosscut by a dark vein in the vicinity of Monforte de Moyuela

As shown by thin sections under the microscope, the vein consists of a light matrix of carbonate minerals, hosting a high amount of black spherical to amoeboidal particles which show gel-like layered structure in the reflective light. The rim towards the dolomite country rock is characterized by pure carbonate crystals having grown perpendicular to the vein's wall. This rim area is free of black particles. A typical feature of the vein is the high amount of gas vesicles.

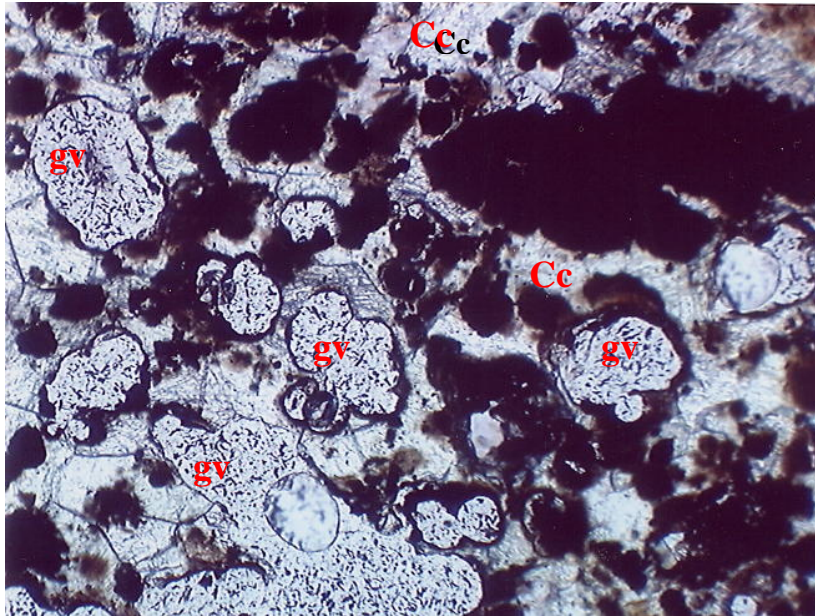


Fig 3: Black vein under the microscope: light matrix of carbonate minerals (Cc), black particles and gas vesicles (gv). Long side of the figure is about 1 mm

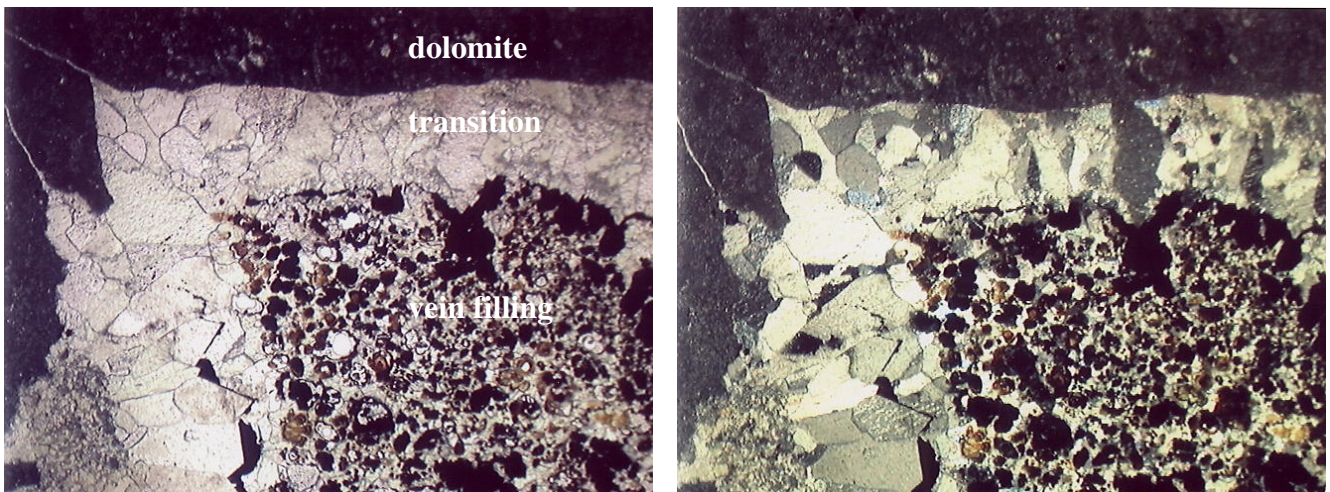


Fig. 4: Rim of the vein towards the dark dolomite country rock, under – and + nicols. The rim area is characterized by a transition zone made up by pure carbonate with crystals having grown perpendicular to the wall of the vein. Long side of the figure is about 4 mm, width of the light transition zone is up to 1 mm

Using a CAMECA SX50 electron microprobe, the dolomite composition of the country rock was verified, small calcitic intercalations are rare. The carbonate crystals of the vein's matrix as well as the light transition zone are, in contrast, pure calcite. The gel-structured black particles turned out to be ore minerals containing Mn and Ba as major elements beside highly variable amounts of light components like H<sub>2</sub>O.

For XRD and XRF investigations on the ore minerals, a sample of the black vein was treated with concentrated HCl to remove the carbonate matrix. The remnant in a powder diffractogram was identified as a very unperfectly crystallized psilomelane with a composition of 63.3 wt.% MnO, 9.1 wt.% BaO and 2.3 wt.% SrO in average, as determined by XRF. In contrast, the untreated vein mainly consists of 48.4 wt.% CaO (~ 86.4 wt.% CaCO<sub>3</sub>), 7.7 wt.% MnO and 0.9 wt.% BaO. The dolomite country rock is composed of 43.3 wt.% MgCO<sub>3</sub> and 54.6 wt.% CaCO<sub>3</sub>.

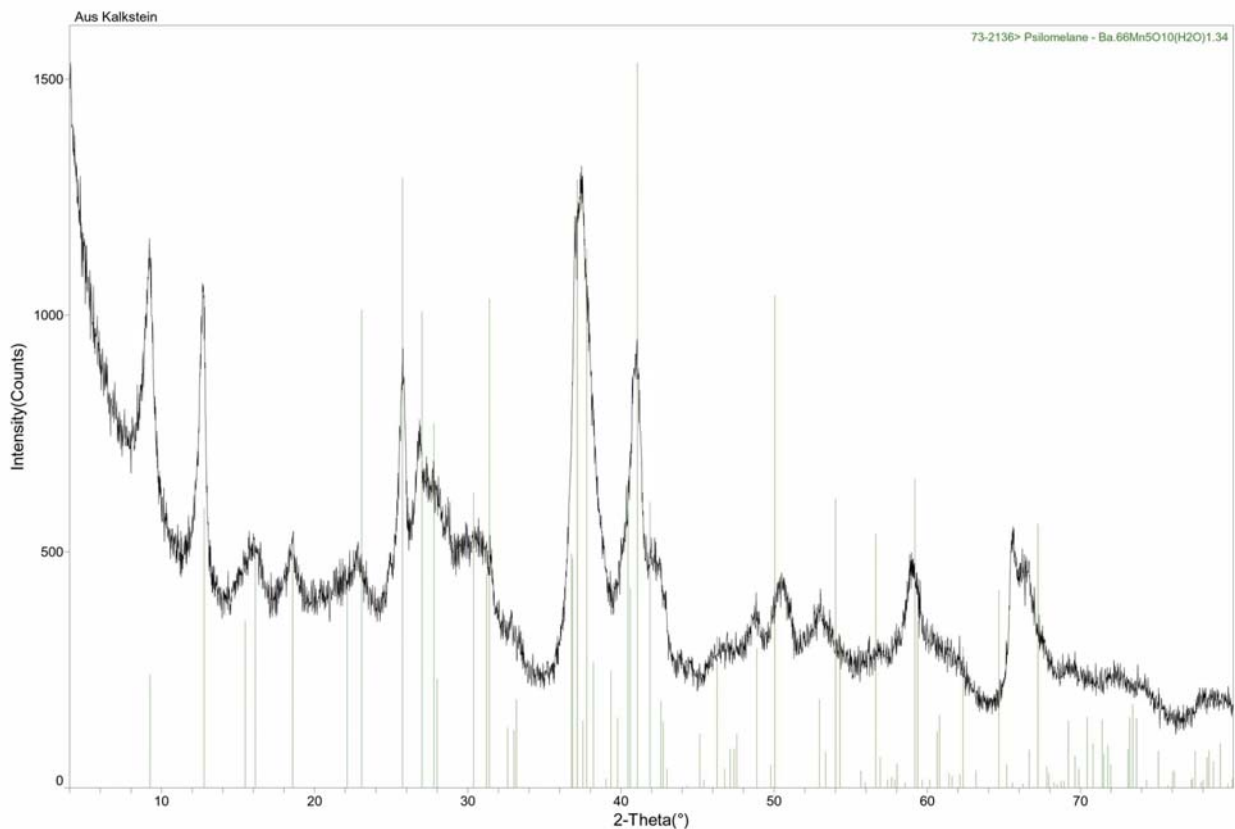


Fig. 5: Powder-diffractogram of the vein remnants after treatment with concentrated HCl. The peaks of the measured diffractogram (black line) clearly fit those of the psilomelane reference diffractogram. The large width of the measured peaks indicates the poor crystallinity of the sample

wt. %	vein	vein without carbonate	country rock dolomite
<b>SiO<sub>2</sub></b>	0.14	0.45	0.43
<b>TiO<sub>2</sub></b>	0.01	0.07	<0.01
<b>Al<sub>2</sub>O<sub>3</sub></b>	<0.10	0.31	0.13
<b>Fe<sub>2</sub>O<sub>3</sub></b>	0.08	0.24	0.4
<b>MgO</b>	0.56	0.42	20.68
<b>CaO</b>	48.39	0.73	30.57
<b>MnO</b>	7.73	63.31	0.05
<b>SrO</b>	0.18	2.32	-
<b>BaO</b>	0.92	9.09	-
<b>Na<sub>2</sub>O</b>	0.26	1	0.15
<b>K<sub>2</sub>O</b>	0.11	0.45	0.03
<b>P<sub>2</sub>O<sub>5</sub></b>	0.01	0.07	0.01
<b>Total</b>	<b>58.39</b>	<b>78.46</b>	<b>52.45</b>
<b>ppm</b>			
<b>V</b>	49	585	11
<b>Co</b>	546	543	<10
<b>Ni</b>	170	837	<5
<b>Zn</b>	33	145	<5
<b>Mo</b>	98	1121	<5
<b>Sr</b>	-	-	99
<b>Ba</b>	-	-	<20

Table 1: X-ray fluorescence analyses of the untreated vein, of the vein remains after treatment with concentrated HCl and of the dolomitic country rock. Cr, Ga, Rb, Y, Zr, Nb, Sn, Pb, Th and U have concentrations below the detection limit in all samples measured

A common occurrence of Mn in carbonates is well known from many geological situations, e.g. the Mn dendrites within carbonate layers of the Malm carbonates in southern Germany. In the Nsuta manganese deposit in Ghana, Mn-enriched marbles even represent the protore for the deposit, which were later upgraded to minable ores by supergene weathering [8]. Therefore, the psilomelane-calcite-vein at first glance is not so astonishing and may be explained by hydrothermal or weathering fluids having circulated through the rocks. Two features, however, do not really match this point of view:

- The very high amount of gas vesicles is totally uncommon for hydrothermal veins and can only be explained by rapid melting-cooling processes with uncomplete degassing of the melt.
- The growth of the calcite crystals in the transition zone between vein filling and country rock perpendicular to the wall of the vein again clearly points to crystal growth from a melt, perpendicular to the cooling front. Similar calcite growth has been observed in amoeba-like carbonate particles embedded in phosphate or silicate glass matrix of suevite samples from the Rubielos de la Cérida and the Nördlinger Ries impact structures, respectively [5, 9]. This texture was interpreted as the result of a quench crystallization of calcite from a carbonate melt [9].

As a conclusion, the psilomelane-calcite-vein of Monforte de Moyuela is interpreted as a former impact-induced Mn-bearing carbonate melt which was injected into cracks of the country rocks at the crater bottom and then rapidly cooled. The source of the carbonate melt is not the Muschelkalk dolomite which forms the present country rock but any pure calcitic carbonate layer within the carbonate-rich stratigraphy of the target area. The source of the manganese is not definitively clear. However, Mn is locally present and occurs only few km from Monforte de Moyuela even in minable concentrations [10]. Also open for discussion remains the formation of the psilomelane which shows clear gel-like structures, which is very unperfectly crystallized and which contains lots of light components like H<sub>2</sub>O. Probably the psilomelane is secondary and formed by replacing a primary Mn mineral.

With this interpretation, the psilomelane-calcite-vein as a special form fits into the large variety of impact-induced breccia dikes of the area around Monforte de Moyuela.

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