

Raman microscopy of prehistoric paintings in French megalithic monuments.

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Supplementary Material

- Fig. S1.** Location of megalithic monuments and stelae studied by μ -RS, SEM/EDS and XPS. (Author: R. Barroso-Bermejo).
- Fig. S2.** The portable Raman microscope BWTEK innoRam 785H in the dolmen 3, orthostat 1, of the tumulus of the Mont-Saint-Michel (Carnac, Morhiban, France).
- Fig. S3.** Barnenez tumulus (Plouezoc'h, Finistère, France).
- Fig. S4.** Plan of the Barnenez tumulus (according to Giot, 1987) indicating the location of the chambers A and H. Red stars: approximate situation of the orthostats with painted decorations that have been analysed (Plan enlarged after P. Bueno Ramírez, R. de Balbín Behrmann, *L'Anthropologie* **2002**; 106, 603).³
- Fig. S5.** Entrance to chamber H of the Barnenez tumulus. (Photo: R. de Balbín-Behrmann)
- Fig. S6.** Interior of the chamber H in the Barnenez tumulus. Red circles: points with painted decorations that have been analysed in situ using a portable μ -RS microscope. White circles: points from which micro-specimens of paint have been removed. (Photographic stitching after elevation in P. Bueno Ramírez et al., *Antiquity* **2015**; 89, 55).⁴
- Fig. S7.** Points of the entrance to the chamber A of the Barnenez tumulus from which micro-specimens of paint have been extracted. (Photo: R. de Balbín-Behrmann).

- Fig. S8.** Entrance to the gallery of Goërem (Gâvres, Morbihan, France).
- Fig. S9.** Plan of the gallery of Goërem. Red star: location of the orthostat P2 that contains painted decorations studied in this article. (Authors: P. Bueno and R. de Balbín-Behrmann).
- Fig. S10.** Points of the orthostat P2 in the gallery of Goërem (Fig. S9) from which micro-specimens of paint (1-4) and the rocky support (5) have been extracted. (Photo: R. de Balbín-Behrmann).
- Fig. S11.** Plan of the dolmen 1 inside the tumulus of Mont-Saint-Michel (Carnac, Morbihan, France). (Author: P. Gouezin). A red star indicates the location of the orthostat in the ceiling of the chamber that contains painted decorations studied in this article. (Authors: P. Bueno-Ramírez and R. de Balbín-Behrmann).
- Fig. S12.** Point (1) of the orthostat in the ceiling of the chamber of the dolmen 1 inside the tumulus of Mont-Saint-Michel (Fig. S11) from which a micro-specimen of paint has been extracted. (Photo: R. de Balbín-Behrmann).
- Fig. S13.** Plan of the dolmen 2 inside the tumulus of Mont-Saint-Michel (Author: P. Gouezin). Red star: location of the orthostat that contains painted decorations studied in this article. (Authors: P. Bueno-Ramírez and R. de Balbín-Behrmann).
- Fig. S14.** Point (1) of the dolmen 2 inside the tumulus of Mont-Saint-Michel (Fig. S13) from which a micro-specimen of paint has been extracted. (Photo: R. de Balbín-Behrmann).
- Fig. S15.** Plan of the dolmen 3 inside the tumulus of Mont-Saint-Michel (Author: P. Gouezin). Red stars: locations of the orthostats that contain painted decorations studied in this article. (Authors: P. Bueno-Ramírez and R. de Balbín-Behrmann).
- Fig. S16.** Points of the dolmen 3 inside the tumulus of Mont-Saint-Michel (Fig. S15) from which micro-specimens of paint have been extracted (white circles 1 and 2) and those studied *in situ* with a portable Raman microscope (red circles 1-6). (Photo: R. de Balbín-Behrmann).
- Fig. S17.** Points (3 and 4) of the dolmen 3, inside the tumulus of the Mont-Saint-Michel (Fig. S15), from which micro-specimens of paint have been extracted. (Photo: R. de Balbín-Behrmann).
- Fig. S18.** Plan of the Dissignac tumulus (Saint-Nazaire, Loire-Atlantique, France). Red star: location of the orthostat with carvings containing possible traces of paint studied in this article (Fig. S19). (Authors: P. Bueno-Ramírez and R. de Balbín-Behrmann).
- Fig. S19.** Orthostat inside the Dissignac tumulus with carvings, Fig. S18. Possible traces of paint in the carvings have been studied *in situ* with a portable Raman microscope (red circles 1-11). (Photo: R. de Balbín-Behrmann).
- Fig. S20.** Orthostats in the chamber of the Mané Rutual dolmen (Locmariaquer, Morbihan, France) with carvings. Point (white circle 1) from which a micro-specimen of paint has been removed. (Photo: R. de Balbín-Behrmann).
- Fig. S21.** Orthostat in the Mané Kerioned B dolmen (Carnac, Morbihan, France) with carvings. Point (white circle 1) from which a micro-specimen of paint has been removed. (Photo: R. de Balbín-Behrmann).
- Fig. S22.** Stela from the megalithic quarry of l'Hirondelle (Bois de Fourgon, Avrillé, Vendée, France). Points (1, 2) from which micro-specimens of paint have been removed. (Photo: R. de Balbín-Behrmann).
- Fig. S23.** Stela from the Neolithic collective grave from Saint-Claude (Bury, Oise, France). Points (1-4) on the front (left) and the back (right) of the stela from which micro-specimens of paint have been removed. (Photo: R. de Balbín-Behrmann).
- Fig. S24.** Representative EDS spectrum of the specimen 1, 2 and 6 extracted from the chamber H of the Barnenez tumulus (Fig. S6). (*) Peak due to copper from the holder used.

- Fig. S25.** XPS spectrum of the specimen 6 of paint from the chamber H of the Barnenez tumulus, expansion of the C 1s region. C 1s peaks from amorphous carbon and carbonate anion are differentiated by a curve fitting of the spectral profile. Label: a.c., amorphous carbon.
- Fig. S26.** XPS spectrum of the specimen 2 of paint from the chamber H of the Barnenez tumulus, expansion of the C 1s region. C 1s peaks from amorphous carbon and carbonate anion are differentiated by a curve fitting of the spectral profile. Label: a.c., amorphous carbon.
- Fig. S27.** Representative μ -RS spectra obtained from the red (specimens 3 and 4) and black paints (specimen 5) used in the chamber H of Barnenez tumulus, Fig. S6 (Supporting Information): a, haematite; b, amorphous carbon; c, amorphous carbon calcite and gypsum; d, gypsum, amorphous carbon and albite. Labels: ac, amorphous carbon; alb, albite; ca, calcite; g, gypsum.
- Fig. S28.** Microphotograph of a particle of the specimen 5 extracted from the chamber H of the Barnenez tumulus (Fig. S6). A black microparticle of charcoal may be observed in the centre of the image.
- Fig. S29.** Microphotographs of colonies of fungi living on painted surfaces of the: (A) chamber H of the Barnenez tumulus; (B) and (C) dolmen 3 of the Mont-Saint-Michel tumulus.
- Fig. S30.** Representative μ -RS spectra of haematite from: a, Bury stela; b, Mont-Saint-Michel tumulus, dolmen 3; c, Mané Rutual dolmen; d, Mont-Saint-Michel tumulus, dolmen 1; e, Mané Kerioned B dolmen; f, L'Hirondelle stela; g, Barnenez tumulus chamber A. Weak and broad bands of amorphous carbon are observed in the spectra from Mané Kerioned B dolmen and l'Hirondelle stela. Label: ac, amorphous carbon.
- Fig. S31.** Representative Raman spectra of components of the dolomitic rock of the l'Hirondelle stela: A, calcite and amorphous carbon; B, dolomite. Labels: ac, amorphous carbon; ca, calcite; *, interference signal from the spectrometer.
- Table S1.** Surface atomic composition detected in paint specimens from different megalithic monuments by XPS. Abbreviations: BCH, Barnenez tumulus, chamber H; GG, gallery of Goërem; MR, Mané Rutual; sp., specimen.

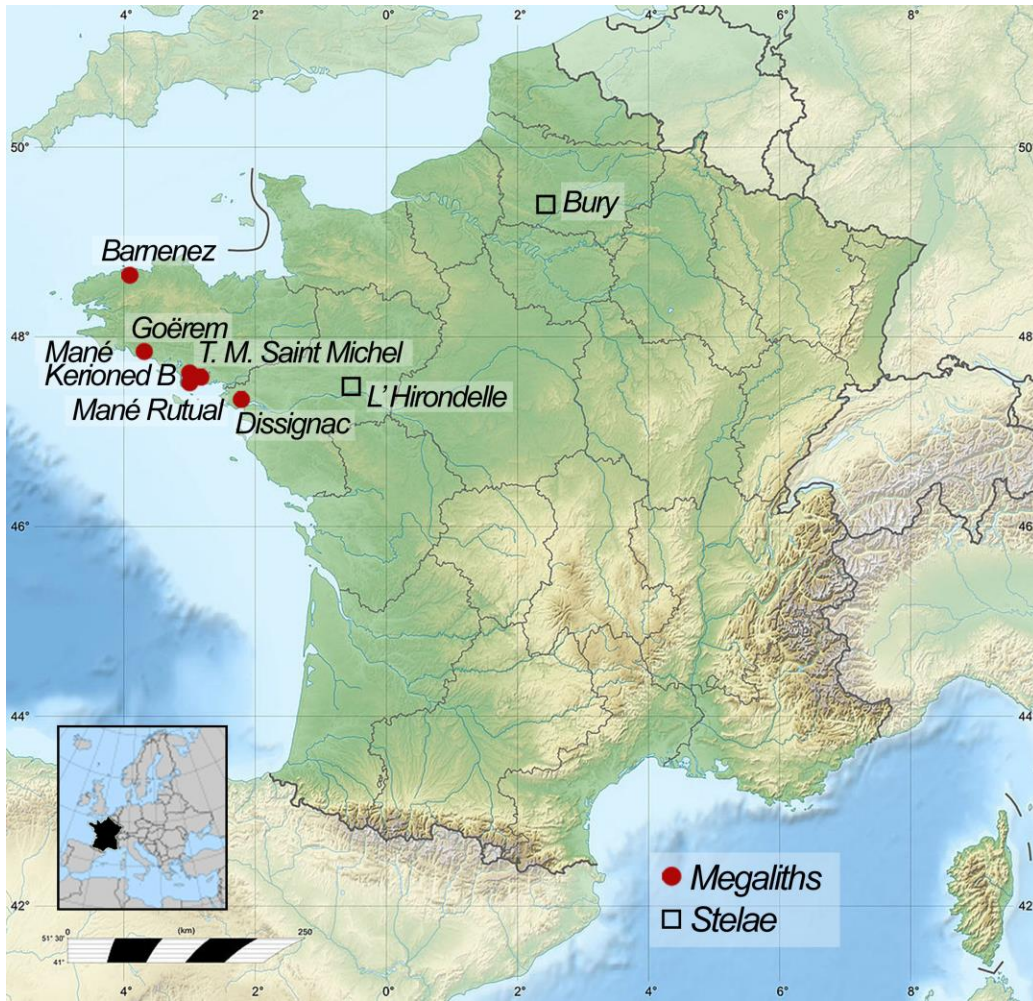


Figure S1. Location of megalithic monuments and stelae studied by μ -RS, SEM/EDS and XPS. (Author: R. Barroso-Bermejo).



Figure S2. The portable Raman microscope BWTEK innoRam 785H in the dolmen 3, orthostat 1, of the tumulus of the Mont-Saint-Michel (Carnac, Morhiban, France).



Figure S3. Barnenez tumulus (Plouezoc'h, Finistère, France).

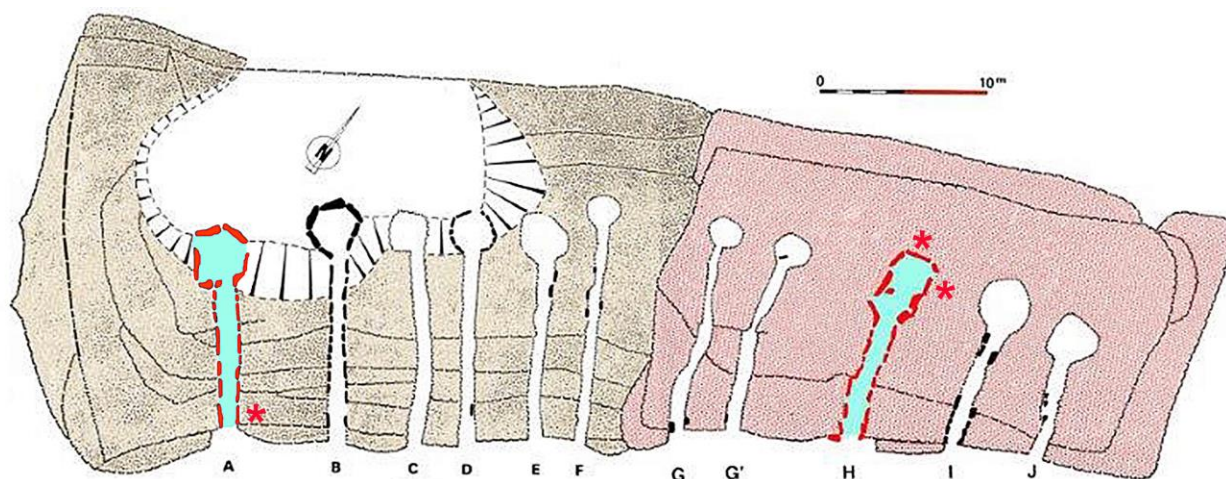


Figure S4. Plan of the Barnenez tumulus (according to Giot, 1987) indicating the location of the chambers A and H. Red stars: approximate situation of the orthostats with painted decorations that have been analysed. (Plan enlarged after P. Bueno Ramírez, R. de Balbín Behrmann, *L'Anthropologie* **2002**; 106, 603).³



Figure S5. Entrance to chamber H of the Barnenez tumulus. (Photo: R. de Balbín-Behrmann)

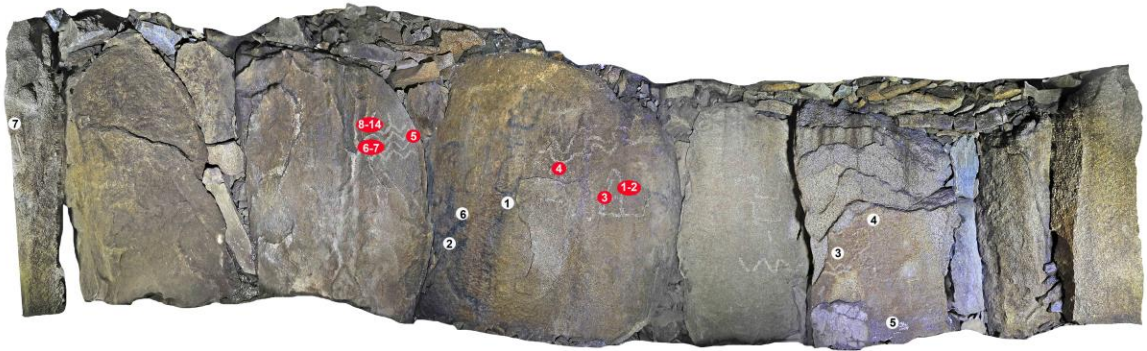


Figure S6. Interior of the chamber H in the Barnenez tumulus. Red circles: points with painted decorations that have been analysed *in situ* using a portable μ -RS microscope. White circles: points from which micro-specimens of paint have been removed. (Photographic stitching after elevation in P. Bueno Ramírez et al., *Antiquity* **2015**; 89, 55).⁴



Figure S7. Points of the entrance to the chamber A of the Barnenez tumulus from which micro-specimens of paint have been extracted. (Photo: R. de Balbín-Behrmann).



Figure S8. Entrance to the gallery of Goërem (Gâvres, Morbihan, France).

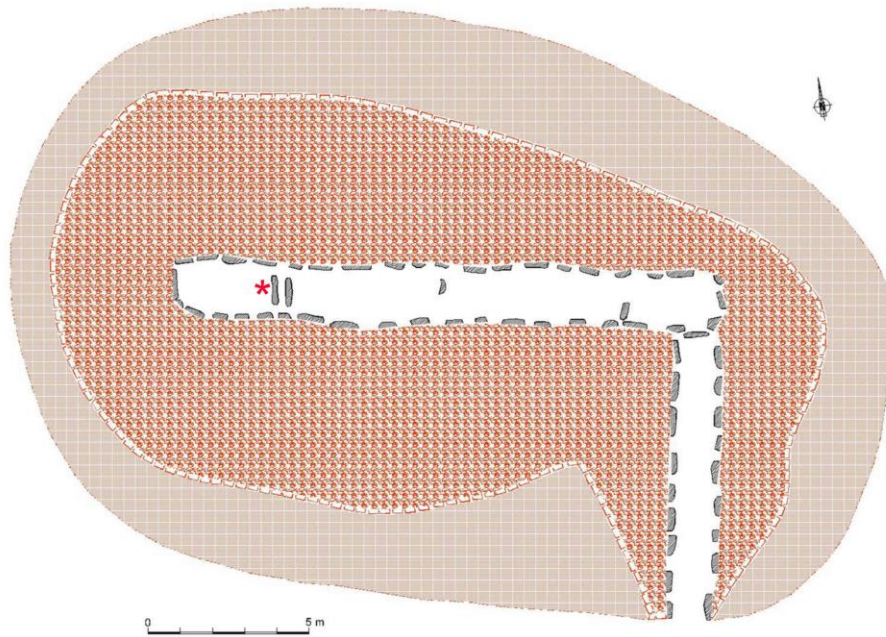


Figure S9. Plan of the gallery of Goërem .Red star: location of the orthostat P2 that contains painted decorations studied in this article. (Authors: P. Bueno and R. de Balbín-Behrmann).



Figure S10. Points of the orthostat P2 in the gallery of Goërem (Fig. S9) from which micro-specimens of paint (1-4) and the rocky support (5) have been extracted. (Photo: R. de Balbín-Behrmann).

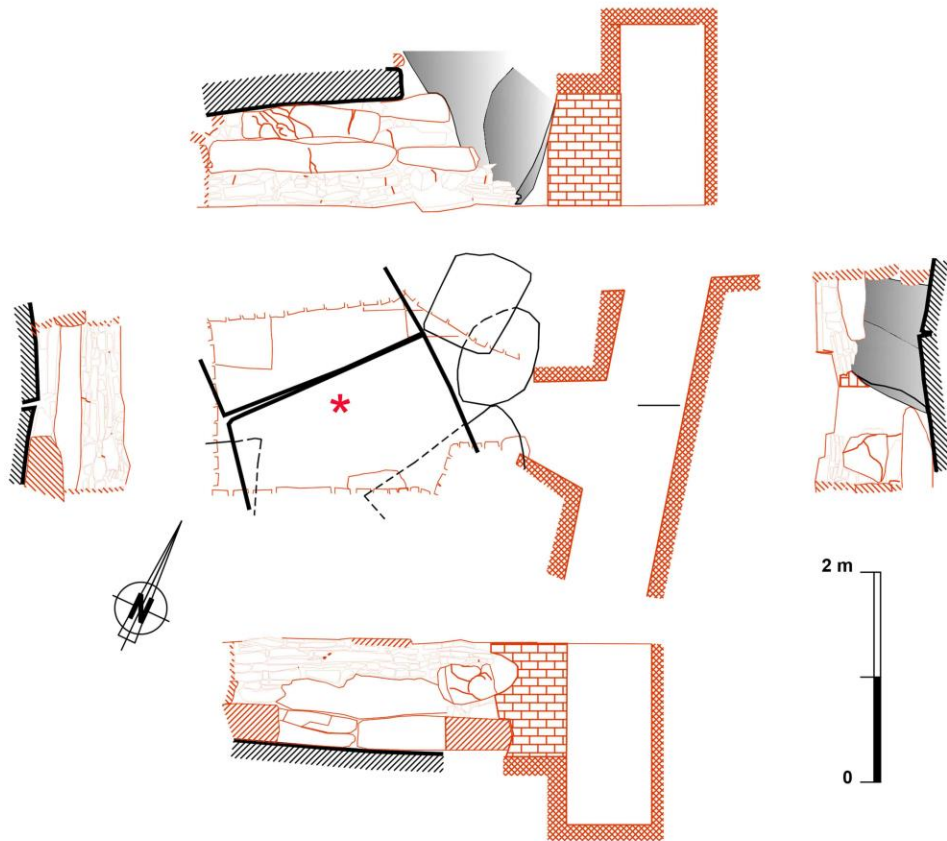


Figure S11. Plan of the dolmen 1 inside the tumulus of Mont-Saint-Michel (Carnac, Morbihan, France). (Author: P. Gouezin). A red star indicates the location of the orthostat in the ceiling of the chamber that contains painted decorations studied in this article. (Authors: P. Bueno-Ramírez and R. de Balbín-Behrmann).



Figure S12. Point (1) of the orthostat in the ceiling of the chamber of the dolmen 1 inside the tumulus of Mont-Saint-Michel (Fig. S11) from which a micro-specimen of paint has been extracted. (Photo: R. de Balbín-Behrmann).

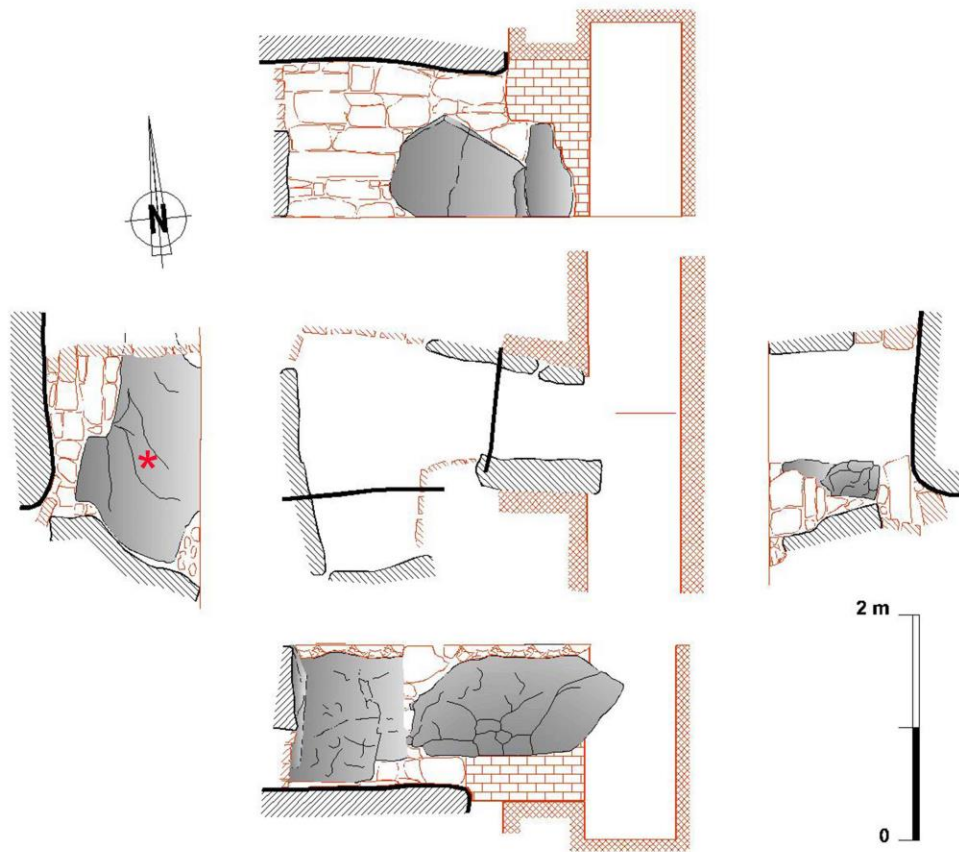


Figure S13. Plan of the dolmen 2 inside the tumulus of Mont-Saint-Michel (Author: P. Gouezin). Red star: location of the orthostat that contains painted decorations studied in this article. (Authors: P. Bueno-Ramírez and R. de Balbín-Behrmann).



Figure S14. Point (1) of the dolmen 2 inside the tumulus of Mont-Saint-Michel (Fig. S13) from which a micro-specimen of paint has been extracted. (Photo: R. de Balbín-Behrmann).

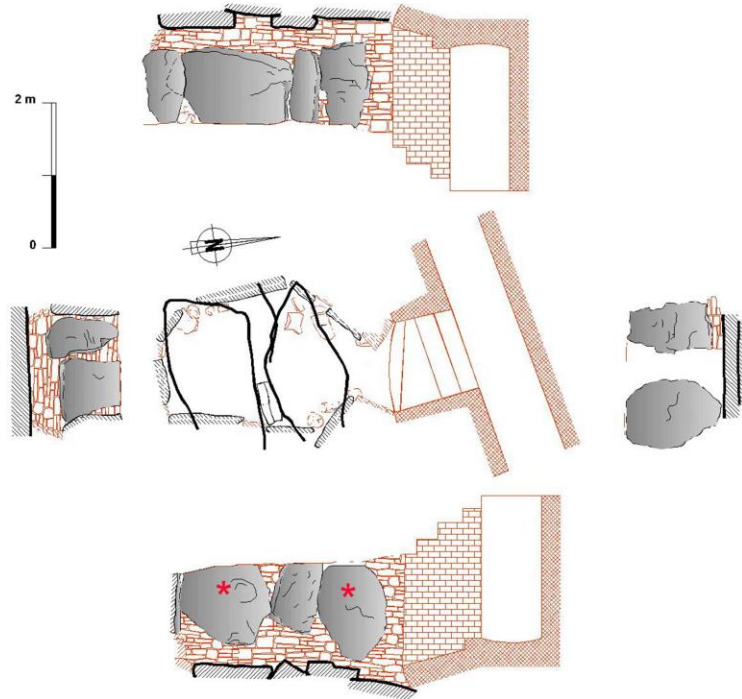


Figure S15. Plan of the dolmen 3 inside the tumulus of Mont-Saint-Michel (Author: P. Gouezin). Red stars: locations of the orthostats that contain painted decorations studied in this article. (Authors: P. Bueno-Ramírez and R. de Balbín-Behrmann).

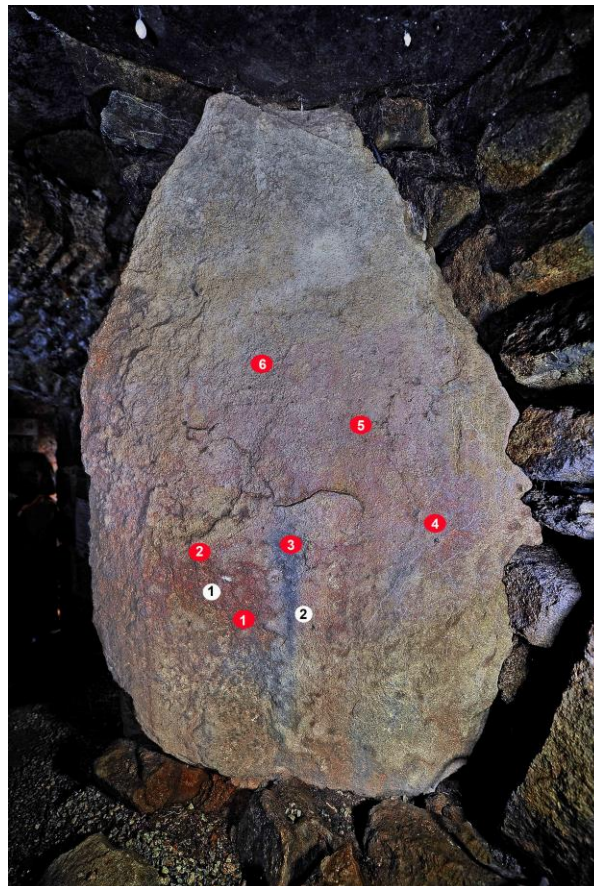


Figure S16. Points of the dolmen 3 inside the tumulus of Mont-Saint-Michel (Fig. S15) from which micro-specimens of paint have been extracted (white circles 1 and 2) and those studied *in situ* with a portable Raman microscope (red circles 1-6). (Photo: R. de Balbín-Behrmann).



Figure S17. Points (3 and 4) of the dolmen 3, inside the tumulus of Mont-Saint-Michel (Fig. S15), from which micro-specimens of paint have been extracted. (Photo: R. de Balbín-Behrmann).

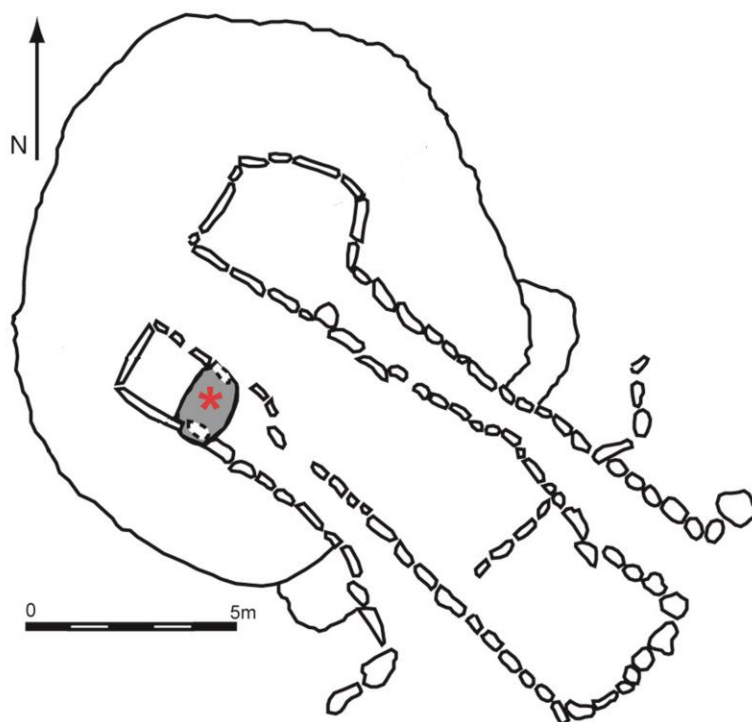


Fig. S18. Plan of the Dissignac tumulus (Saint-Nazaire, Loire-Atlantique, France). Red star: location of the orthostat with carvings containing possible traces of paint studied in this article (Fig. S19). (Authors: P. Bueno-Ramírez and R. de Balbín-Behrmann).



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Fig. S20. Orthostats in the chamber of the Mané Rutual dolmen (Locmariaquer, Morbihan, France) with carvings. Point (white circle 1) from which a micro-specimen of paint has been removed. (Photo: R. de Balbín-Behrmann).



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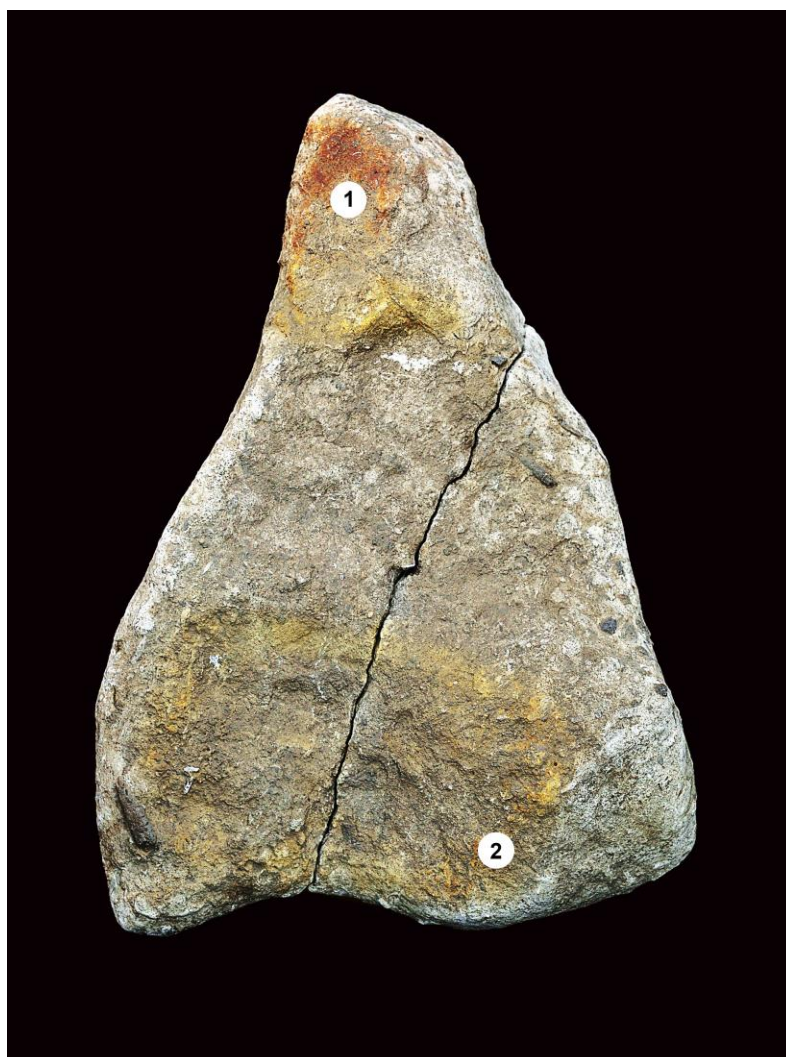


Fig. S22. Stela from the megalithic quarry of l'Hirondelle (Bois de Fourgon, Avrillé, Vendée, France). Points (1, 2) from which micro-specimens of paint have been removed. (Photo: R. de Balbín-Behrmann).

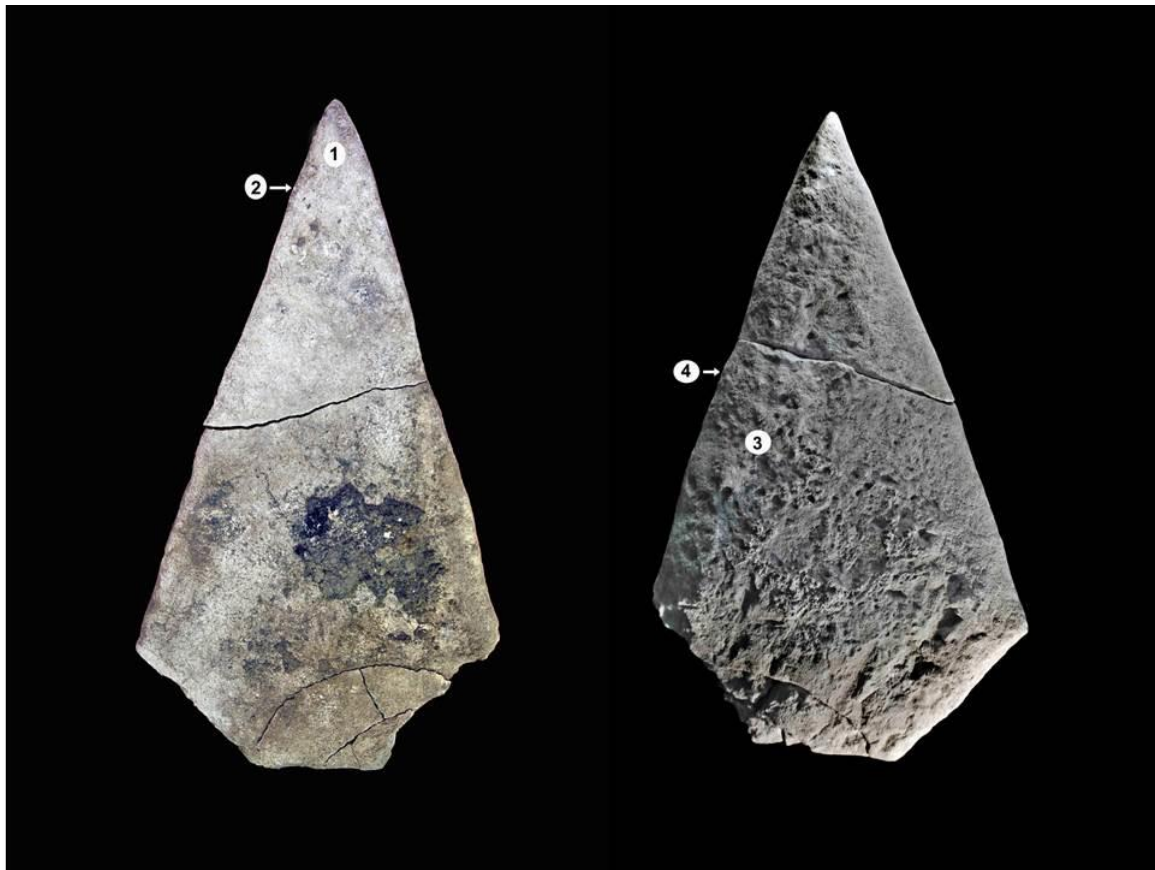


Fig. S23. Stela from the Neolithic collective grave from Saint-Claude (Bury, Oise, France). Points (1-4) on the front (left) and the back (right) of the stela from which micro-specimens of paint have been removed. (Photo: R. de Balbín-Behrmann).

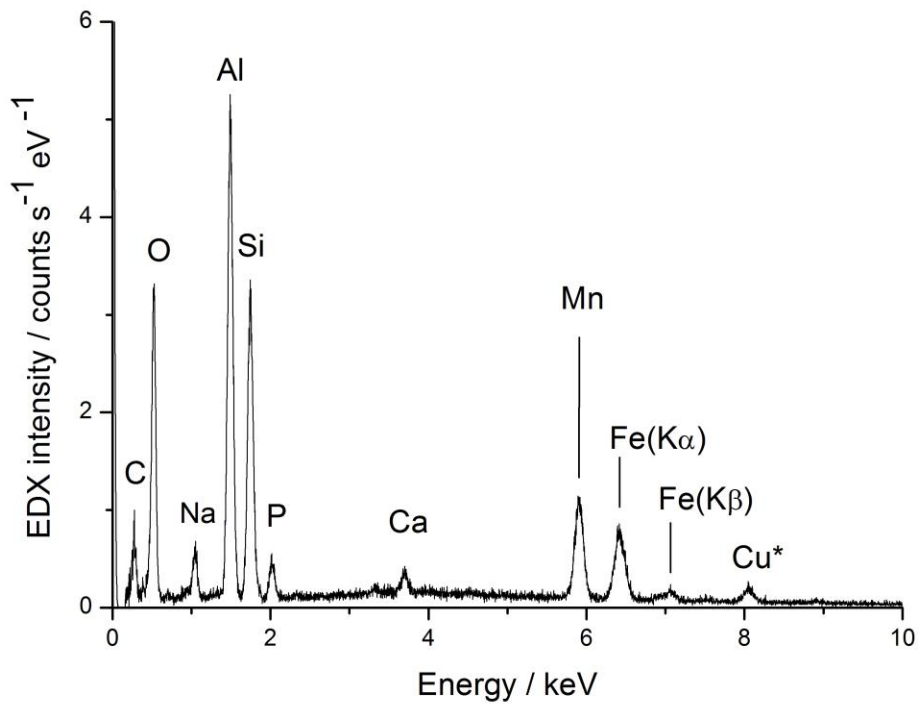


Fig. S24. Representative EDS spectrum of the specimens 1, 2 and 6 extracted from the chamber H of the Barnenez tumulus (Fig. S6). (*) Peak due to copper from the holder used.

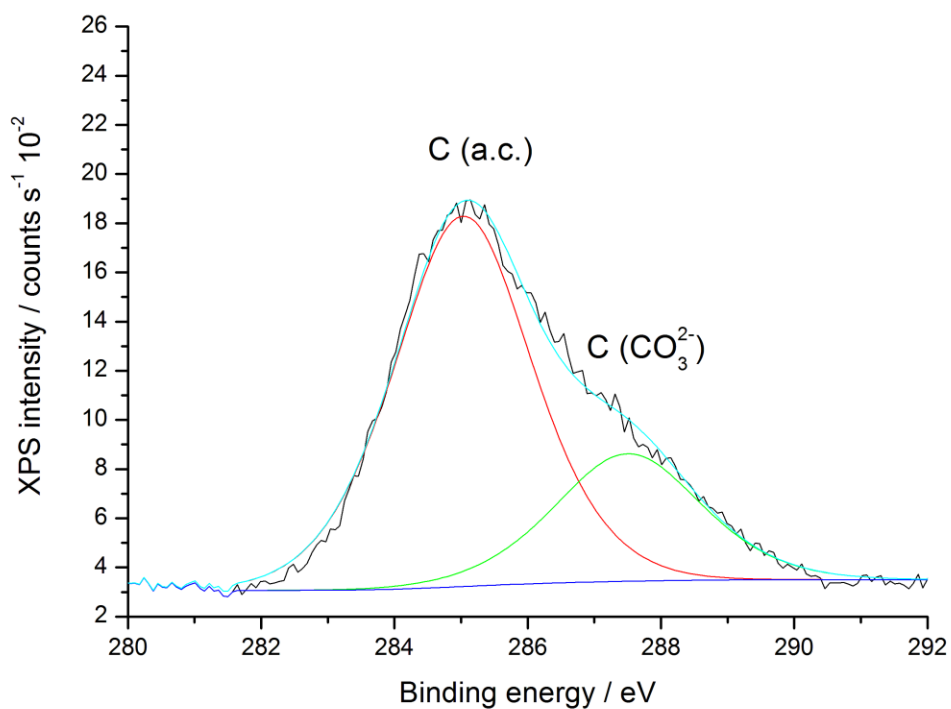


Fig. S25. XPS spectrum of the specimen 6 of paint from the chamber H of the Barnenez tumulus, expansion of the C 1s region. C 1s peaks from amorphous carbon and carbonate anion are differentiated by a curve fitting of the spectral profile. Label: a.c., amorphous carbon.

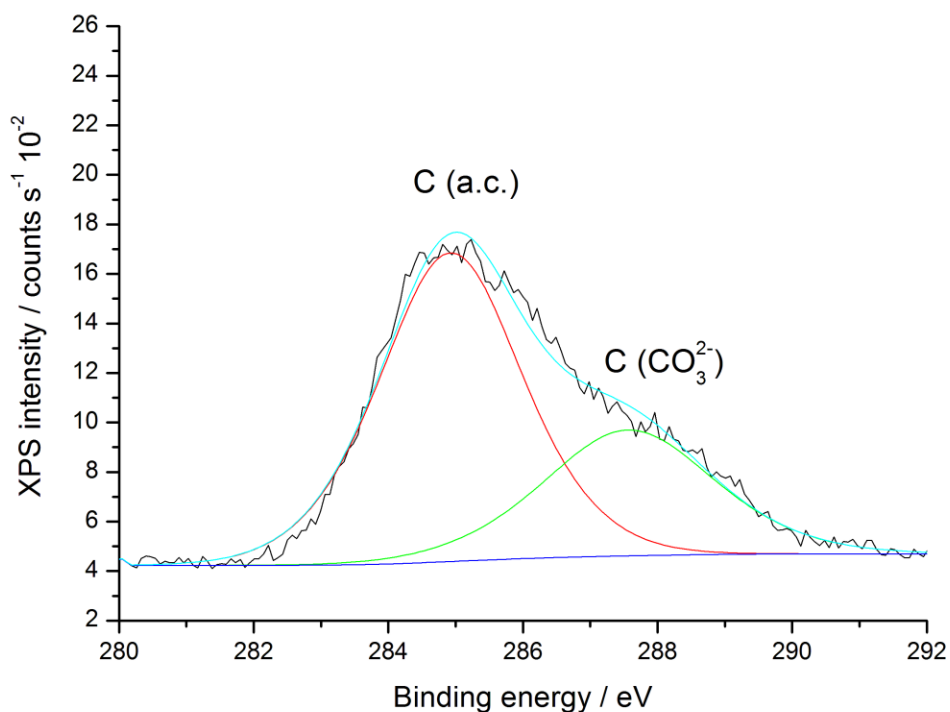


Fig. S26. XPS spectrum of the specimen 2 of paint from the chamber H of the Barnenez tumulus, expansion of the C 1s region. C 1s peaks from amorphous carbon and carbonate anion are differentiated by a curve fitting of the spectral profile. Label: a.c., amorphous carbon.

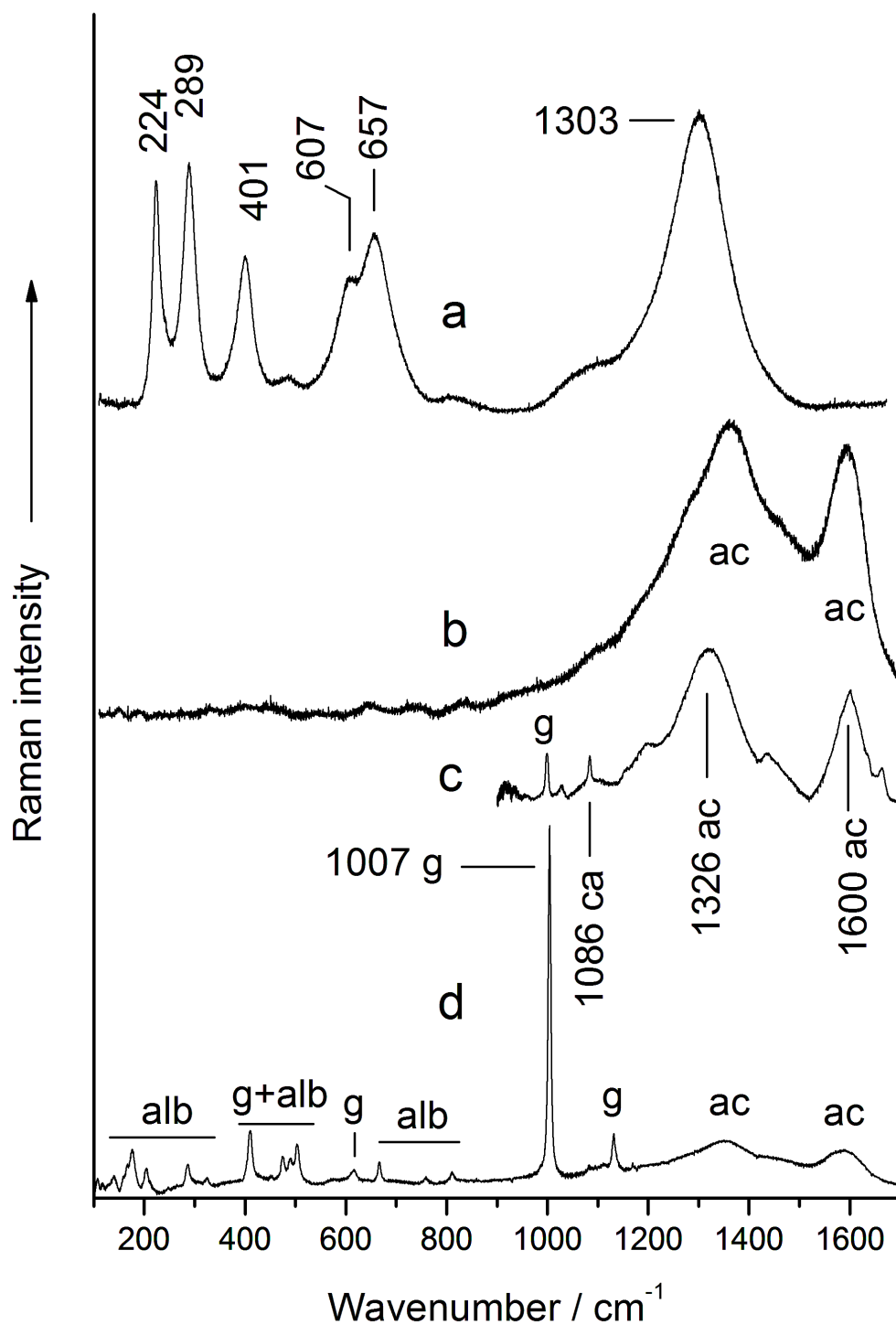


Fig. S27. Representative μ -RS spectra obtained from the red (specimens 3 and 4) and black paints (specimen 5) used in the chamber H of Barnenez tumulus, Fig. S6 (Supporting Information): a, haematite; b, amorphous carbon; c, amorphous carbon calcite and gypsum; d, gypsum, amorphous carbon and albite. Labels: ac, amorphous carbon; alb, albite; ca, calcite; g, gypsum.

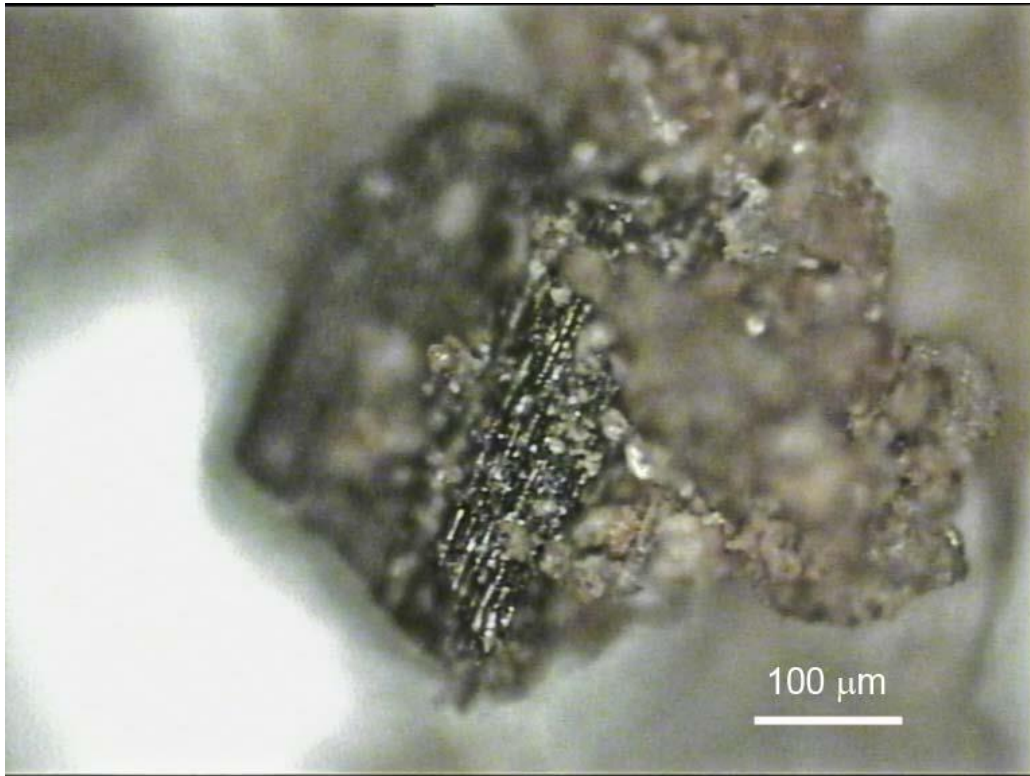


Fig. S28. Microphotograph of a particle of the specimen 5 extracted from the chamber H of the Barnenez tumulus (Fig. S6). A black microparticle of charcoal may be observed in the centre of the image.

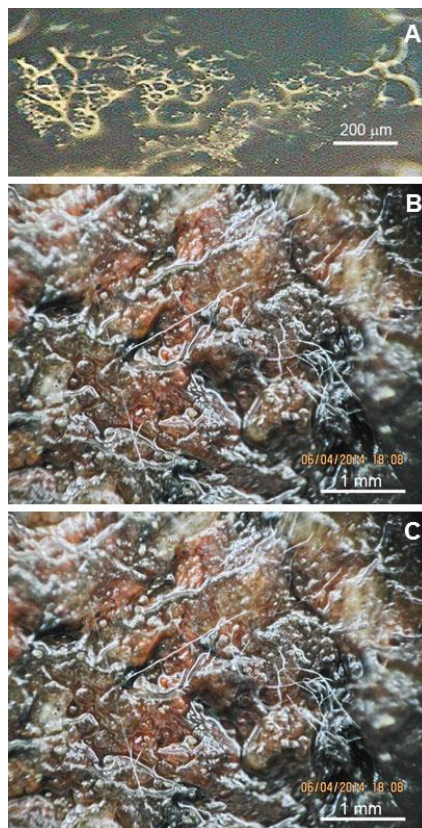


Fig. S29. Microphotographs of colonies of fungi living on painted surfaces of the: (A) chamber H of the Barnenez tumulus; (B) and (C) dolmen 3 of the Mont-Saint-Michel tumulus.

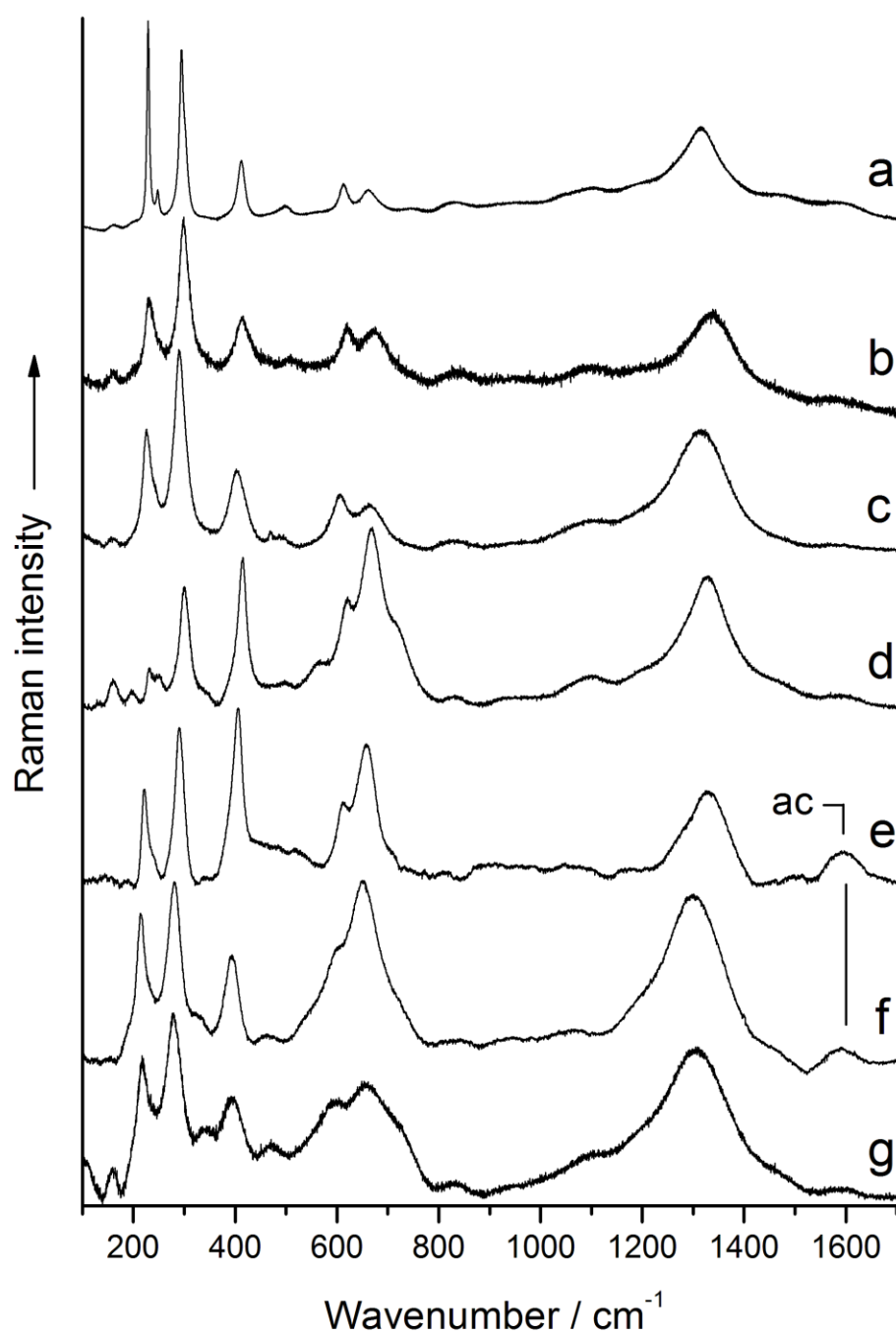


Fig. S30. Representative μ -RS spectra of haematite from: a, Bury stela; b, Mont-Saint-Michel tumulus, dolmen 3; c, Mané Rutual dolmen; d, Mont-Saint-Michel tumulus, dolmen 1; e, Mané Kerioned B dolmen; f, l'Hirondelle stela; g, Barnenez tumulus chamber A. Weak and broad bands of amorphous carbon are observed in the spectra from Mané Kerioned B dolmen and l'Hirondelle stela. Label: ac, amorphous carbon

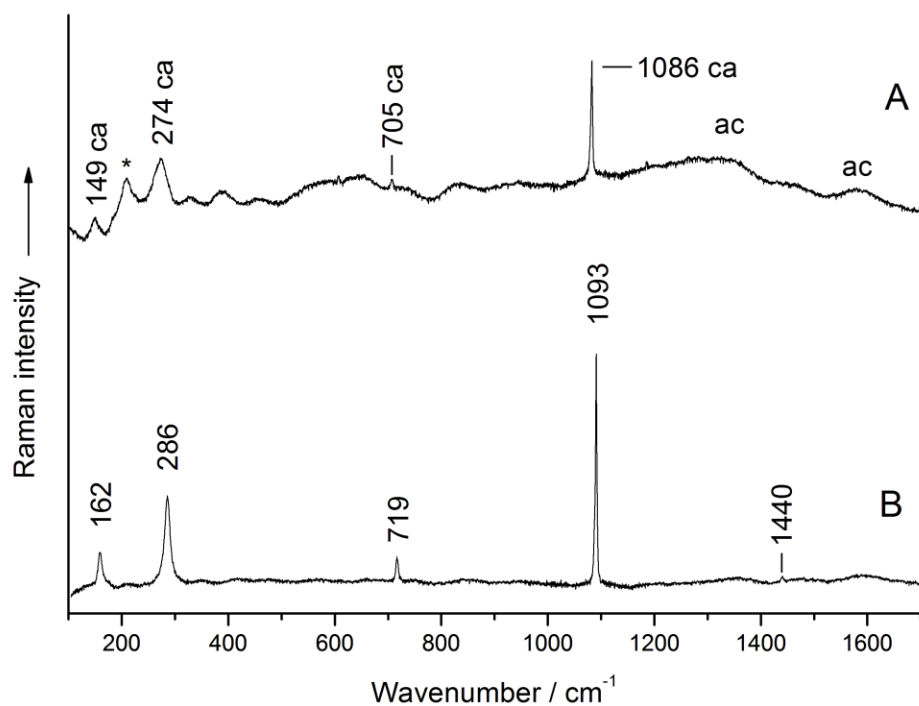


Fig. S31. Representative Raman spectra of components of the dolomitic rock of the l'Hirondelle stela: A, calcite and amorphous carbon; B, dolomite. Labels: ac, amorphous carbon; ca, calcite; *, interference signal from the spectrometer.

Table S1. Surface atomic composition detected in paint specimens from different megalithic monuments by XPS. Abbreviations: BCH, Barnenez tumulus, chamber H; GG, gallery of Goërem; MR, Mané Rutual; sp., specimen.

Element / %	C	O	N	Al	Si	Ca	Fe	P	S	F	Mn	K	Na
BCH, sp. 6	49.7	28.0	5.7	8.3	3.2	1.1	0.4	1.1	0.9	1.5	0.2	0.0	0.0
BCH, sp. 2	34.0	41.9	2.5	10.9	7.5	0.3	0.2	1.6	0.7	0.0	0.3	0.0	0.0
GG, sp. 2	11.5	48.6	1.0	12.2	23.1	1.2	0.7	0.7	0.0	0.0	0.0	0.8	0.3
MR, sp. 1	42.9	31.6	3.6	4.7	8.8	0.9	0.6	2.5	1.2	3.1	0.0	0.0	0.0