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FRONT COVER
Lorenzo Monaco, *The Coronation of the Virgin* (NG 215, 1897, 216) (detail of Plate 1, p. 44)

TITLE PAGE
Carlo Crivelli, *The Dead Christ supported by Two Angels* (NG 602; detail), after cleaning and restoration

Occurrences of the Purple Pigment Fluorite on Paintings in the National Gallery

MARIKA SPRING

THE MINERAL FLUORITE (calcium fluoride) Loccurs in nature in a variety of colours, including purple, pink, blue, green and yellow. Its use as a flux for smelting metals, and in the glass-making industry, was described already in the sixteenth century by the German metallurgist Georgius Agricola. He goes on to say 'moreover, from Fluores they can make colours which artists use'.1 Purple fluorite has been found used as a pigment but, so far, relatively rarely and on works from a limited geographical area and period of time. Virtually all the occurrences that have been published are on panel paintings, polychrome sculpture and wall paintings from the Tyrol and Southern Germany, where there are particularly good deposits of purple fluorite. They date from the period 1470-1520, coinciding with the golden age of silver and copper mining in these areas – fluorite is found as a gangue mineral with the ores of these metals.² Several of the paintings in the National Gallery on which fluorite has been found fit in with this pattern of occurrences but, significantly, a number are on paintings which are not from Alpine areas of Europe (see Table 1).

Michael Pacher, who worked mainly in Bolzano

in the Tyrol, used fluorite on his small painting of The Virgin and Child Enthroned (NG 5786) for the greyish-purple colour of the architecture.3 In a crosssection of paint from the architecture (Plate 1) both colourless and purple particles of fluorite are visible, many with a characteristic rectangular shape due to the cubic crystal structure of the mineral. The sample also contains other colourless material such as calcite, quartz, and various silicaceous minerals which occur in deposits with fluorite.4 Calcium fluoride is inherently colourless; the colour in mineral deposits is believed to result from defects in the crystal lattice generated by impurities such as rare earth elements or radioactive minerals close to the deposit. 5 Bulk samples of the mineral often have a veined appearance, with colourless and coloured fluorite interspersed. The deep purple variety, with a colour strong enough to produce a pigment of acceptable tinting strength when ground to a powder, is generally found in conjunction with radioactive minerals such as uranium ores.6

The painting by Pacher is rather unusual in that fluorite was mixed only with lead white, and used in the uppermost paint layer, apparently specifically for its distinctive cold greyish-purple colour. More



Plate I Michael Pacher, The Virgin and Child Enthroned with Angels and Saints (NG 5786). Cross-section of a sample from the mordant-gilded crozier of the bishop saint, showing the fluorite-containing greyish-purple paint of the architecture below the gilding. Original magnification 600x; actual magnification 525x.

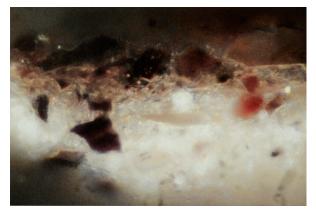


Plate 2 Albrecht Altdorfer, Christ taking Leave of his Mother (NG 6463). Cross-section of a sample from Christ's purple-red drapery. Veined purple particles of fluorite are visible, mixed with red lake and lead white. Original magnification 940x; actual magnification 825x.

Table 1 Occurrences of fluorite on paintings in the National Gallery

Artist	Title	Place of origin	Date	Location of fluorite on the painting
Michael Pacher	The Virgin and Child Enthroned with Angels and Saints (NG 5786)	Tyrol	Probably 1475?	Architecture and canopies; purple fluorite mixed with lead white. ¹
Wolf Huber	Christ taking Leave of his Mother (NG 6550)	Feldkirch?	c.1519	Purple-grey drapery of the Holy Woman second from the left figure group; purple fluorite mixed with lead white, azurite and red lake. ²
Albrecht Altdorfer	Christ taking Leave of his Mother (NG 6463)	Regensburg?	c.1520	Christ's purple-red drapery; purple fluorite mixed with red lake and lead white in underpaint, glazed with red lake prepared with dyestuff from the kermes insect. ³
Master of Cappenberg (Jan Bagaert)	Christ before Pilate (NG 2154)	Wesel	C.1520	Christ's purple-grey drapery; purple fluorite mixed with lead white. ¹
Jan Gossaert	A Man holding a Glove (NG 946)	Breda or Veere?	1530-2	Pink area of sleeve; purple fluorite, ⁴ lead white and a little red lake.
Netherlandish School	A Man with a Pansy and a Skull (NG 1036)	?	c.1535	Man's purple-grey sleeve; purple fluorite mixed with lead white, smalt and azurite.4
'Ysenbrandt'	The Magdalen in a Landscape (NG 2585)	Bruges	152085	Pink robe of the angel holding a crucifix; purple fluorite ⁴ mixed with red lake and lead white.
Style of 'Ysenbrandt'	The Entombment (NG 1151)	Bruges?	c.1550	Sky paint; small amount of purple fluorite ⁴ mixed with lead white, smalt and azurite.
After Quinten Massys	The Virgin (NG 295.2)	Antwerp	After 1503 ⁶	Virgin's blue drapery; fluorite ⁴ and lead white underpaint beneath ultramarine.

¹ Fluorite identified by X-ray diffraction, in agreement with JCPDS file 4-864.

result was confirmed recently by HPLC, carried out by Jo Kirby.

² I am grateful to Mark Richter for identification of fluorite in this sample by EDX analysis in the scanning electron microscope. The sample is illustrated in 'Wolf Huber's Christ taking leave of his Mother', National Gallery Technical Bulletin, Early Northern European Painting, 18, 1997, ed. L. Campbell, S. Foister and A. Roy, p. 105, Plate 83.

³ Kermes identified by TLC, published in A. Smith and M. Wyld, 'Altdorfer's "Christ taking leave of his Mother", National Gallery Technical Bulletin, 7, 1983, p. 62. The

⁴ Identified by EDX analysis in the scanning electron microscope. I am grateful to Aviva Burnstock for the use of the EDX equipment at Kings College, University of London, and for her assistance.

⁵ Dendrochronology was carried out by Peter Klein on the panel of NG 2585. The last ring present was from 1491, giving a plausible creation date of after 1508.

⁶ Dendrochronology was carried out by Peter Klein on NG 295.2. The last ring present was from 1478, giving a plausible creation date of after 1503.

often, it has been found mixed with red lake and used in underpaint, as it is on Albrecht Altdorfer's Christ taking Leave of his Mother (NG 6463; Plate 2) and on Wolf Huber's version of the same subject (NG 6550).7 It was perhaps used as an extender for the relatively expensive red lake, or to give a purplered colour without using blue pigments, which were also expensive.



Plate 3 Jan Gossaert, A Man holding a Glove (NG 946). Cross-section of a sample from the pink sleeve; purple fluorite mixed with lead white over a lead white priming layer. Original magnification 800x; actual magnification 700×.



Plate 4 Jan Gossaert, A Man holding a Glove (NG 946), c.1530-2. Panel, 24.4 × 16.8 cm.

These three works were all painted in Alpine regions, close to well-known European sources of purple fluorite. The other six paintings in the National Gallery on which it has been found, however, are not by painters from the Tyrol or Southern Germany (Plates 3–8). Five of the paintings are from the Netherlands. Jan Gossaert's Portrait of a Man holding a Glove (NG 946) was painted around 1530 when Gossaert was working mainly in the northern part of the Netherlands, perhaps in Breda. 8 The Magdalen in a Landscape (NG 2585) attributed to 'Ysenbrandt' was almost certainly painted in Bruges,9 as was The Entombment (NG 1151), which has been classified as style of 'Ysenbrandt'. 10 The Virgin (NG 295), probably after Quinten Massys, is likely to have been painted in Antwerp. The Portrait of a Man with a Pansy and a Skull (NG 1036) has been dated around 1535 on the basis of the costume, but it is not known where it was painted. 11 It is close in style to portraits by Jan van Scorel, who was based in Utrecht. 12 It is worth noting, also, that the purple fluorite on these paintings is weaker in colour and of smaller particle size than on the paintings from Alpine regions.

There is no obvious link between these paintings, making it difficult to draw any conclusions about the pattern of use of fluorite in the Netherlands. In the occurrences on paintings from Alpine areas it appears to have been used because it was a local material. It is, in fact, a common mineral - the most abundant fluorine mineral in the earth's crust - and although the deep purple variety is less common, good deposits are also found elsewhere in Europe, notably in the Massif Central in France (Puy-de-Dôme), Asturias in Spain (La Collada) and the Pyrenees.¹³ A detailed search of the mineralogy literature shows that there are deposits in several places in the Ardennes in the southern part of the Low Countries. 14 The same region was the source of a zinc ore which was being mined in this period for the brass industry, so it is feasible that the veins of fluorite were also being exploited. 15 These paintings all date from the first part of the sixteenth century, a time when many artists - including, it is thought, Jan Gossaert – made the journey across the Alps on their way to Italy. 16 They may have come across the use of fluorite as a pigment during their travels. Jan van Scorel was in Austria long enough to paint an altarpiece for the parish church of Obervellach, and while he was there he is known to have used local painting materials.¹⁷ It is also possible that fluorite was traded across Europe - there were well-established trading links with the copper and silver mines in Alpine areas, the same mines which are thought



Plate 5 'Ysenbrandt', Magdalen in a Landscape (NG 2585). Cross-section of a sample from the pink drapery of the angel holding a crucifix. Small purple particles of fluorite are visible, with red lake and lead white, in the uppermost layer. The paint of the angel lies over the green foliage, which contains some green copper sulphate pigment. Original magnification 750x; actual magnification 660×.



Plate 6 'Ysenbrandt', Magdalen in a Landscape (NG 2585). Detail of the angel holding a crucifix.

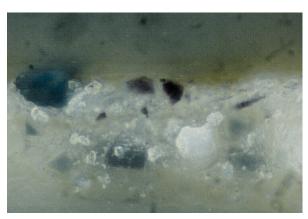


Plate 7 Style of 'Ysenbrandt', The Entombment (NG 1151). Cross-section of a sample from the greyish-blue sky, containing fluorite, azurite, smalt and lead white. Original magnification 940×; actual magnification 660×.

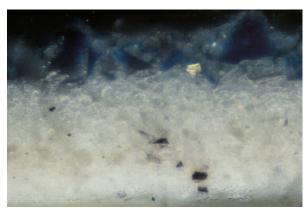


Plate 8 After Quinten Massys, The Virgin (NG 295.2). Cross-section of a sample from the Virgin's blue robe; a layer containing lead white and a small amount of purple fluorite lies beneath ultramarine. Original magnification 750x; actual magnification 660x.

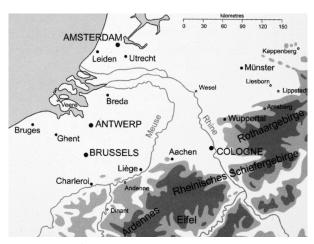


Fig. 1 Map of the Netherlands and Westphalia (modern coastline).

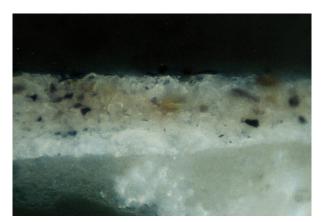


Plate 9 Master of Cappenberg, Christ before Pilate (NG 2154). Cross-section of a sample from Christ's brownish-purple drapery. The uppermost layer contains lead white and a small amount of purple fluorite. Original magnification 600x; actual magnification 525x.

to be the source of the fluorite used by artists working in the Tyrol.¹⁸

The other painting on which fluorite was found is attributed to the Master of Cappenberg, now generally identified as Jan Bagaert. Christ before Pilate (NG 2154) was almost certainly originally part of one of the wings of the high altar at the abbey church in Liesborn, Westphalia, in which case it would have been painted in Wesel in the western part of Westphalia, where Jan Bagaert's studio was located, as documents exist concerning the transport of the panels.¹⁹ Again, it is rather surprising to find fluorite on a Westphalian panel - here in Christ's brownishpurple drapery (Plates 9 and 10) - as it is far from the Alpine areas of Germany. Wesel is close to the modern Dutch border, as near to the deposits of fluorite in the Ardennes as Antwerp or Bruges. There are also small deposits of deep violet fluorite in

Westphalia, for example in the Casparizeche mine near Arnsberg and in the Schiefergebirge mountains, east of Wesel but close to the towns of Cappenberg and Liesborn (Fig. 1).20

Fluorite was not the only local material to have been used on the painting by Pacher. Dolomite (calcium magnesium carbonate) was used for the ground layer on the back of the panel, and has also been found in the ground layers of many of the other works from Alpine areas on which fluorite has been found.²¹ The use of fluorite was reported on a sculpture by the Augsburg master Sebastian Loscher (1513), polychromed by Hans Burgkmair, together with natural mineral posnjakite (green copper sulphate) in areas of green paint, yet another natural material which has been found relatively rarely as a pigment.²² Interestingly, green copper sulphate was used for the background of the Portrait of a Man with a Pansy and a Skull, for the foliage on Ysenbrandt's Magdalen in a Landscape, and for the background of Gossaert's Portrait of a Man holding a Glove.²³ It has also been reported on other Netherlandish paintings of the early sixteenth century, including works by Jan Massys, Lucas van Leyden and Jan van Scorel, with much discussion about whether it is natural or artificial in origin.24 In Ysenbrandt's Magdalen in a Landscape the green copper sulphate is almost certainly a natural mineral, as the paint also contains colourless material such as quartz and other silicates which occur with the natural mineral. As with fluorite, the pigment could have been imported to the Netherlands from elsewhere, or could have come from a more local source such as the small deposit of posnjakite that exists in the Ardennes, in the north of the Meuse valley.²⁵ Another material which is not usually used on paintings was found on the Master of Cappenberg's Christ before Pilate (Plate 10). The red-brown layer on which the gold leaf of Christ's halo is laid contains a black pigment that proved to be a bismuth compound, probably bismuth sulphide, mixed with red earth.26 The use of bismuth sulphide, or bismuthinite as the mineral is called, as a pigment is extremely rare – it has been found only on a few sixteenth-century paintings from Italy.²⁷

The use of fluorite as a pigment was clearly more widespread than has so far been thought. The group of paintings examined here are not particularly well documented, making it difficult to draw definite conclusions about when, where and why fluorite was used. There are, however, some intriguing connections between them, such as the use of other rarely encountered pigments which are found as natural minerals, particularly green copper sulphate, in other



Plate 10 Master of Cappenberg, Christ before Pilate (NG 2154). Detail showing the figure of Christ.

areas of the paintings. All the Netherlandish paintings on which fluorite has been found date from the first part of the sixteenth century, a period at which there does seem to have been a change in the taste of colour on paintings, evolving towards less saturated, more subtle hues. The journey to Italy via Alpine regions that many artists made at this time may also have had an important effect on their choice of materials: some aspects of Jan van Scorel's technique, for example, are thought to have been influenced by his travels.²⁸ Fluorite may also have been used on paintings from some of the other localities where there were notable deposits of the purple variety and it seems certain that further examples will come to light.

Acknowledgements

Lorne Campbell and Susan Foister provided much help with the art-historical aspects of this paper, particularly the references. I would also like to thank Michele Marincola, Andreas Burmester, Hubert Paschinger and Helmut Richard for useful discussion on the subject of fluorite on Tyrolean and South German works. I am also grateful to Mark Richter for analysis of the sample from the painting by Huber, and to Aviva Burnstock for assistance with the analysis of the National Gallery samples.

Notes and References

- 1 G. Agricola, De Re Metallica, trans. by H.C. Hoover and L.H. Hoover, New York 1950. Agricola's discussion of 'stones which melt easily in the fire' in Bermannus and De Natura Fossilium is reproduced in note 15, p. 380. The properties described point to some of these stones being fluorite.
- 2 M. Richter and R. Fuchs, 'Violetter Flußspat', Restauro, 5, 1997, pp. 316–23. Richter and Fuchs gathered together all the published occurrences and reported some more examples of the use of fluorite. Richter has also, more recently, identified fluorite on a painting by Cranach, see G. Heydenreich, 'Artistic Exchange and Experimental Variation: Studies in the Workshop Practice of Lucas Cranach the Elder', Painting Techniques: History, Materials and Studio Practice, Preprints of the IIC Dublin Congress, 7-11 September 1998, ed. A. Roy and P. Smith, London 1998, pp. 112-14. It seems to have been used by Cranach only when he was working in Vienna. It has also been reported on a gothic sculpture from Hungary, see Aktuell, Restauro, 5, 1998, p. 297. A few more examples on paintings from the Tyrol were published in M. Koller and M. Vigl, 'Großgmainer Altar', 500 Jahre Meister von Großgmain, exh. cat., Großgmain bei Salzburg, 1-22 August 1999, pp. 93-4.
- 3 See also the article on Pacher in this issue of the Technical Bulletin.
- 4 C.S. Hurlbut, Dana's Manual of Mineralogy, 18th edn.,

reprinted 1971, New York and London, p. 312. Fluorite is usually found in hydrothermal veins, where it can be the chief mineral or a gangue mineral with metal ores, especially lead, silver and zinc. Other minerals that have been found associated with it include calcite, dolomite, gypsum, celestite, barite, quartz, galena, sphalerite, cassiterite, topaz, tourmaline and apatite. EDX analysis on the sample from the painting by Pacher revealed that many of the colourless impurities were quartz and calcite. Some silicaceous material was also present (Si, Al, K detected, together with a small amount of Ti, Fe and Ca).

- 5 The cause of the colour is discussed in Richter and Fuchs, cited in note 2.
- 6 A. Chermette, La Fluorite, Paris 1986, p. 24.
- 7 Fuchs and Richter, cited in note 2.
- 8 H. Pauwels, H.R. Hoetink and S. Herzog, Jean Gossaert dit Mabuse, exh. cat. Museum Boymans van Beuningen, Rotterdam, and Groeningemuseum, Bruges 1965, p. 379. Quittances were signed by Gossaert in Breda, 27 March 1532, and Turnhout, 19 May 1532. His wife and family probably resided at Veere, however.
- 9 T.-H. Borchert, 'Adrian Isenbrandt', Bruges et la Renaissance, De Memling à Pourbus, Notices, exh. cat., Memlingmuseum, Bruges 1998, pp. 65-7, No. 39.
- 10 R. Billinge, 'Links with Schongauer in Three Early Netherlandish Paintings in the National Gallery', Looking Through Paintings, Leids Kunsthistorisch Jaarboek *XI*, ed. E. Hermens, 1998, pp. 88–9.
- 11 M. Davies, National Gallery Catalogues, The Early Netherlandish School, 3rd edn., London 1968. For Gossaert see p. 61, for Massys p. 92, for Netherlandish School (NG 1036) p. 137 and for Ysenbrandt pp. 177–9.
- 12 Personal communication with Lorne Campbell.
- 13 Chermette, cited in note 6, pp. 42, 92, 96.
- 14 J. Mélon, P. Bourguignon and A.-M. Fransolet, Les Minéraux de Belgique, Belgium 1976, pp. 102-4. There are many deposits of fluorite in the Ardennes massif, between Liège and Charleroi. A detailed list of the locations, and the colours of the fluorite found there, are given in this publication. See also R.F. Vochten, M.K. Van Doorselaer and H. Dillen, 'Fluorite from Seilles, Andenne, Belgium: Colouration, fluorescence and a remarkable crystal geometric discolouration phenomenon', Zeitschrift-Deutsche Gemmologische Gesellschaft, 43, June 1994, pp. 73-84. The Seilles deposit is in the north of the Meuse Valley, where it occurs with limestone and dolomite.
- 15 J. Day, 'Brass and Zinc in Europe from the middle ages until the mid-nineteenth century', 2000 Years of Zinc and Brass, British Museum Occasional Paper no. 50, ed. P.T. Craddock, London 1990, rev. edn. 1998, pp. 133-56. The production of brass goods in the fifteenth and sixteenth centuries was concentrated in Dinant, Bouvignes and other smaller communities along the Meuse because deposits of calamine (zinc carbonate), a necessary raw material, were found there. Zinc ore of particularly high quality was found in the Eifel near Aachen. The importance of Aachen as a centre for

- brass production increased after the sack of Dinant by the Duke of Burgundy in 1466.
- 16 Pauwels, Hoetink and Herzog, cited in note 8, p. 374. Embassy of Philip of Burgundy to Rome via Trent and Verona, over the Brenner pass, recorded in December 1508, when Jan Gossaert was in his service.
- 17 M. Faries and M. Wolff, 'Landscape in the early paintings of Jan van Scorel', Burlington Magazine, November 1996, pp. 724-33. Dolomite (calcium magnesium carbonate) was found as a ground layer on Jan van Scorel's Adoration of the Magi, Art Institute of Chicago. It is painted on a fir panel, which was used as a support mainly in Alpine regions.
- 18 E. Westermann, 'Copper production, trade and use in Europe from the end of the fifteenth century to the end of the eighteenth century', Copper as Canvas, two centuries of masterpiece paintings on copper 1575-1775, exh. cat. published by Phoenix Art Museum and Oxford University Press, New York and Oxford 1999, pp. 117-23.
- 19 M. Levey, National Gallery Catalogues. The German School, London 1959, pp. 65-70. R. Brandl, 'The Liesborn altar-piece, a new reconstruction', Burlington Magazine, cxxxv, 1993, pp. 180-90. Brandl proposes that NG 2154 and NG 263 were part of the wings of the Liesborn Altarpiece, and are therefore the panels documented as having been sent to Jan Bagaert in Wesel for painting. The forthcoming National Gallery Catalogue of German paintings before 1800 will provide more concrete technical evidence in support of this proposal.
- 20 H. Hatton, 'Flußspatvorkommen auf der Casparizeche bei Arnsberg/Westfalen', Der Aufschluss, Vol. 30, 6, June 1979, p. 210. Violet as well as light yellow fluorite is found near Valentinite (Sb₂O₃) and Berthierite (FeSb₂S₄) in the antimony deposits of Arnsberg, Westphalia.
- 21 Richter and Fuchs, cited in note 2, mention several paintings on which fluorite has been found which have a ground layer containing dolomite.
- 22 A. Burmester and J. Koller, 'Der heilige Alexius: naturwissenschaftliche Untersuchung der Farbfassung Hans Burgkmairs' Der heilige Alexius im Augsburger Maximilianmuseum', Arbeitsheft 67, Bayerisches Landesamt Für Denkmalpflege, Munich 1994, pp. 38-47. The sculpture by Sebastian Loscher of 1513 was polychromed at a later date by Hans Burgkmair. Fluorite was used in purple areas and a mixture of green copper salts in green areas of paint, including copper sulphate of the posnjakite and langite form, which can occur together in natural deposits. The presence of quartz led to the conclusion that a natural mineral had been used.
- 23 Identified by EDX analysis on a cross-section. The foliage paint on The Magdalen in a Landscape attributed to 'Ysenbrandt' (NG 2585) contains some quartz (only Si detected in some particles by EDX) and other silicaceous minerals in addition to copper sulphate, therefore the pigment is almost certainly natural in origin.
- 24 P.F.J.M. Hermesdorf et al., 'The Examination and restoration of the Last Judgement by Lucas van Leyden',

Lucas van Leyden – studies, Nederlands Kunsthistorisch *Jaarboek*, 29,1978, Haarlem 1979, p. 407, note 144. Posnjakite was identified on a sample from the Last *Judgement* by X-ray diffraction. Posnjakite was also reported on a painting by Jan van Scorel (identified by X-ray diffraction), see J.R.J. van Asperen de Boer, 'Examen scientifique des peintures du groupe Jan van Scorel', Jan van Scorel d'Utrecht, exh. cat. Musée Central Utrecht and Musée de la Chartreuse, Douai 1977, pp. 54-5. Long blue-green crystals of posnjakite, Cu₄(SO₄)(OH)₆.H₂O, were also identified by X-ray diffraction on two paintings by Jan Massys (Saint Jerome, Rouen, Musée des Beaux-Arts, David and Bathsheba, Paris, Louvre) and a copper sulphate pigment was found on Judith and the Head of Holofernes (Paris, Louvre), although the particular form of copper sulphate could not be confirmed, see E. Martin and M. Eveno, 'Contribution to the study of old green copper pigments in easel paintings', 3rd International Conference on non-destructive testing, microanalytical methods and environment evaluation for study and conservation of works of Art, October 1992, Viterbo, pp. 781-91. At the end of this paper the possibility that it may be artificial is suggested. This is discussed in more detail in E. Martin, A. Duval and M. Eveno, 'Une famille de

- pigments verts mal connue', Techne, 2, 1995, pp. 76-9.
- 25 R. Van Tassel, 'Occurrence de Posnjakite en Belgique', Annales de la Société Géologique de Belgique, 100, 1977, pp. 203-4.
- 26 Bismuth was detected in the black pigment by EDX analysis. One of the major Bi peaks overlaps with the S peak in the EDX spectrum therefore it was not possible to confirm that it was bismuth sulphide, which occurs naturally as the mineral bismuthinite.
- 27 C. Seccaroni, 'Some Rarely Documented Pigments. Hypothesis and Working Observations on Analyses Made on Three Temperas by Correggio', Kermes, Year XII, No. 34, January-April 1999, pp. 41-4. Bismuth metal was used for bismuth painting, a technique used mostly for decorating caskets and boxes which developed in Switzerland and Southern Germany in the sixteenth century. See R. Gold, 'Reconstruction and Analysis of Bismuth Painting', Painted Wood: History and Conservation, Proceedings of a Symposium at Williamsburg, Virginia, 11-14 November 1994, ed. V. Dorge and F. Carey Howlett, 1998, pp. 166-78.
- 28 M. Faries, 'Some results of the recent Scorel research: Jan van Scorel's definition of landscape in design and color', in Color and Technique in Renaissance Painting, Italy and the North, ed. M.B. Hall, New York 1987, p. 92.