Note from the Making and Knowing Project:

This essay was written for “The Art Technological Source,” an 8-week graduate course at the University of Amsterdam offered by Dr. Marjolijn Bol in 2015 and 2016 to students enrolled in an MA program in either Technical Art History or Conservation and Restoration. Students worked on various recipes from BnF Ms. Fr. 640 on the following five topics: 1) tracing and painting on glass, 2) yellow dyes and their applications, 3) dragon’s blood, 4) painters’ varnishes, and 5) sieves.

This is an un-edited student paper that relies on an earlier state of the Making and Knowing Project’s transcription and translation of Ms. Fr. 640. For an updated version of the text, see:

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A Complex Material Made Simple:

Examining the Author-Practitioner’s Practical Understanding of Alum in BnF Ms. Fr 640

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Alum was one of the first chemicals manufactured on an industrial scale in Europe because of its utility in many different processes. The author-practitioner of the late-sixteenth-century French manuscript BnF Ms. Fr 640 shows the versatility of alum as a material in medieval recipes by using it in several recipes in his manuscript, ranging from casting to making varnishes. Alum also plays a key role in manufacturing lake pigments such as scudegrun, a yellow lake pigment made by precipitating the dye extracted from weld onto a colorless substrate. The author-practitioner includes this recipe for scudegrun on fol. 10r: "It is made in Lyon from the juice of weld mixed with chalk or better yet with ceruse, which is appropriate for tempera and oil."[1] However, a reconstruction of this recipe[2] led to the realization this recipe does not explicitly mention the key ingredient of alum or another substance that can form a complex with the pigment molecule to precipitate it out of solution.

This annotation seeks to elucidate the author-practitioner's understanding of alum as a material that was used for pigment-making and dyeing. Examining the author-practitioner's understanding of alum may give insight into how this scudegrun recipe was intended to be interpreted, and whether the omission of a critical ingredient like alum was deliberate. Further context for these parts of the manuscript will be provided by modern research concerning alum in pigment-making and dyeing, and by the use of alum in natural pigment recipes contemporary to BnF Ms. Fr 640. Extensive research has been done on natural dyes and pigments and the use of alum in their making process—especially of note is Jo Kirby, Maarten van Bommel, and André Verhecken's work on natural pigment-making, which was used to formulate the initial experiment and acted as a reference for context for the recipe.[3] This annotation seeks to draw on that extensive research and focus it specifically on the author-practitioner's understanding of alum to examine the way that sixteenth-century craftsmen like the author-practitioner related to their materials.

In the process of reconstructing this recipe, the recipe was attempted both with and without alum to test if the recipe would produce the intended colored pigment as written. The resulting pigments from this experiment can be seen in fig. 1 after being mixed with linseed oil and applied to a gesso board.

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[1] *Original French:* "Se faict avecq de la fleur de genest fort bouillié dans de l'eau, y mettant suffisament de l'alum, puys de la ceruse." (fol. 10r)

[2] The reconstruction of the scudegrun recipe on fol. 10r was executed in the context of the Art Technological Source class for the University of Amsterdam Masters in Conservation and Restoration. The reconstruction of these recipes was done in association with the Making and Knowing Project at Columbia University, which is studying and annotating BnF Ms. Fr. 640. For more details concerning the full experiment conducted, refer to "Field notes from the reconstruction of scudegrun pigment (fol. 10r) from BnF Ms. Fr. 640."

[3] See: Jo Kirby, Maarten van Bommel and André Verhecken, *Natural Colorants for Dyeing and Lake Pigments: Practical Recipes and Their Natural Colorants for Dyeing and Lake Pigments* (London: Archetype, 2014), 28. Another important source is Dominique Cardon's work on the sources and processes used for natural dyes, which are closely related to natural lake pigments, and which analyses the mordants used in their production, as collected in *Natural Dyes: Sources, Tradition, Technology and Science* (London: Archetype, 2007). Further identification of lake pigments and the alum used in their manufacturing process can be found in comprehensive reference works such as Eastaugh's *The Pigment Compedium: A Dictionary of Historical Pigments* (London: Routledge, 2007).

Fig. 1: Linseed oil paint samples made from weld lake pigments. In all cases, the pigment was extracted from weld by soaking the weld overnight and then boiling the weld for half an hour. The pigments were manufactured from recipe 5a from *Natural Colorants for Dyeing and Lake Pigments: Practical Recipes and Their Historical Sources* as a guide. From top: paint from pigment precipitated with only chalk, with reference of pure chalk mixed with oil to the right; paint from pigment precipitated with chalk and alum; paint from pigment precipitated with chalk and alum, with more concentrated weld juice. Note the lack of color in the pigment precipitated with only chalk, as the recipe for scudegrun on fol. 10r would seem to specify.

The pigment obtained from following the recipe without alum produced a cream-colored paint with only a slight color difference from pure chalk mixed with paint, while the attempts of the recipes with alum produced a mustard-yellow pigment that is likely more representative of the intended color for scudegrun. However, other recipes for scudegrun in the manuscript do specifically mention alum as an ingredient in the recipe: “It is made with the broom flower well boiled in water, putting in it enough alum, then some ceruse.” (fol. 63v) The presence of alum in this recipe shows that the author-practitioner was aware of the need for alum in precipitating a similar yellow lake pigment.

When the pigment is precipitated from the mixture onto chalk using alum, the aluminium hydroxide forms a complex with the dye extracted from the plant[4], as in a regular lake, which is then precipitated on the chalk.[5] As our experiment above proves, the chalk substrate alone is not enough to hold the dye—a pigment like this requires alum to complex with the dye molecules. The alum acts as a

[4] Weld yields luteolin, a flavonoid dye molecule. See: Dominique Cardon, *Natural Dyes: Sources, Tradition, Technology and Science* (London: Archetype, 2007), 678.
[5] Daniel V. Thompson, *The Materials and Techniques of Medieval Painting* (New York: Dover Publications, 1956), 119.

coordination metal that forms a complex with the dye particles in a process similar to mordant dyeing.[6] As for the bond between the alum-dye complex and the chalk substrate, Kirby suggests in weld pigments with chalk substrates, the dye molecule-alum complex may be attached to the substrate mostly by adsorption, rather than complexation.[7] The lake that results from this combination is more opaque than a regular lake, because it contains not only the transparent hydrated alumina particles complexed with the dye that are in a lake precipitated only with alum, but also the more opaque calcium sulphate and unreacted calcium carbonate particles.[8] In the case of weld lakes, the opacity lent to the weld lake was sometimes preferred by medieval color-makers, leading to recipes that precipitated the color onto opaque materials, such as calcium salts (from chalk, marble, and egg shells), lead white, flour, and ochres.[9]

When making lake pigments, alum works analogously to mordants in dyes, and making lake pigments was often tied to the dyeing industry because of the overlap in the materials used.[10] The author-practitioner seems to have know that the processes to make lake pigments and the processes to make dyes are related to each other, because fol. 57v mentions that "Florence lake is better than lake from Flanders because in Florence they make the best dyes."[11] The author-practitioner's assessment of Florence's dyes and pigments is likely accurate, as Florence was known in the fifteenth and sixteenth centuries for their high-quality kermes and madder dyed textiles, and clippings of these textiles were used to make red lakes by extracting the dye from with an alkali and then precipitating the dye with alum.[12] The same passage also mentions that the addition of too much alum into the dye solution will make this Florentine red lake more purple or violet.[13] This might not be entirely accurate: an excess of alum in making the pigment would likely not cause the purplish color that the author-practitioner

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[6] The alum molecule forms a complex with the dye molecule by attaching to neighboring C=O and C-OH groups, forming an insoluble polymeric hydroxide. See: Kirby, *Natural Colorants for Dyeing and Lake Pigments,* 25. See also: Lars Ohrstrom, "Alum," *Royal Society of Chemistry*.

[7] Kirby, *Natural Colorants for Dyeing and Lake Pigments,* 34.
Pink brazilwood lakes also used opaque white materials such as chalk, marble dust, powdered eggshells, or white lake. Thompson claims that in the making of brazilwood lake, the white material is effectively dyed by the pigment-making process, where the alum forms a complex between the substrate and the dye molecule. See: Thompson, *The Materials and Techniques of Medieval Painting,* 119

[8] Kirby, *Natural Colorants for Dyeing and Lake Pigments*, 77.
Thompson, *The Materials and Techniques of Medieval Painting*, 79, 80.

[9] Kirby, *Natural Colorants for Dyeing and Lake Pigments,* 77.
Thompson, *The Materials and Techniques of Medieval Painting,* 188.
The color produced by this process was known as *stil de grain* in France, and recipes such as the one in the later 18th century *Traité de la peinture au pastel* (1788) make sure to distinguish between the lake created by only adding alum to the solution and the *stil de grain* created by adding chalk. See: Paul-Romain Chaperon. *Traité de la peinture au pastel* (Paris: Defer de Mainsonneuve, 1788), 82.

[10] Kirby, *Natural Colorants for Dyeing and Lake Pigments*: 28, 73.

[11] Original French: "La laque de Florence est meilleure que celle de Flandres car à Florence se font les meilleures taincture."

[12] Robert Chenciner, *Madder Red: A History of Luxury and Trade* (London: Routledge, 2000), 154, 180.
Cennino Cennini, *Cennino Cennini's Il Libro Dell' Arte,* ed. Lara Broeke (London: Archetype, 2015), 69.

[13] "To make a beautiful flesh color, the reddest and brightest lake is the best, because those that are purple and violet as a result of the addition of too much alum make a flesh color that appears as if one is very cold."

Original French: "Pour faire belle carnation la laque la plus rouge & plus vive est la meilleure, car celle qui tient du purpurin & violet par la mixtion de trop d'alum faict la carnation co{mm}e d'un qui ha grand froit." (fol. 57v) mentions.[14] However, this observation does show that the author-practitioner likely understood that the process of lake pigment involved the use of a mordant like alum to deposit a color onto the substrate, and that a change in the mordant material that could result in a color change. The author-practitioner also identifies alum as a material that is necessary in the process of dyeing wood green or red on fol. 76r, speciying old urine, madder, and rock alum as ingredients for dyeing wood red.[15] The madder used in this recipe was also used in dyeing fabrics and making pigments,[16] as mentioned above, and alum is a vital mordant ingredient in any of these dyeing processes. This recipe further suggests that the author has a familiarity with different kinds of plant material dyes and the methods needed fix the dyes onto different substrates.

The author-practitioner also has knowledge of how best to process alum from its raw form to a form that would be usable in his recipes. On fol.107r, where alum is used in a casting process, he specifies that "it is difficult to grind stone alum, and it cannot be sieved, you must grind it on a marble slab. […] white [stone alum] powder that apothecaries sell is good, it is easy to crush it into a mortar, use the pestle slowly, that way you will make [the stone alum] very fine."[17] Both of these passages suggest that the author-practitioner has experience grinding the alum from its raw form to a usable powder appropriate to the recipes. Other recipes for pigments also mention a fine-ground alum, such that this knowledge of how to process the alum would have been applicable to pigment-making.[18] The author-practitioner also mentions quality as a factor in choosing alum from an apothecary, showing an awareness of different grades of alum and the way they influence the quality of the final product.[19]

[14] Cennini specifies in making red lake pigments that only a little alum is necessary to obtain a bright red, and excess alum resulted in an opaque pink color in a modern reconstruction was carried out by Lara Broeke, Anne Servais, and William Whitney in 2014. See: Cennini, *Cennino Cennini's Il Libro Dell' Arte*, 235.
It is more likely that this colour change may have occurred due to the addition of iron or copper to an alum mordant mixture, which was a common way of shifting a madder or kermes dye to a more purple shade. See: Cardon, *Natural Dyes: Sources, Tradition, Technology and Science*, 40.
[15] "Making Wood Red: Take one quart of old urine, three ounces of madder, and one ounce of rock alum, put all of the ingredients into your pot. Then follow the previously described green technique."
Original French: "Pour faire boys rouge: Prenés une carte d'urine vieilhe et trois onces de garance & une once d'alung de glace, et metrés le tout dans v{ost}re pot, & faictes comme du verd."
The urine likely functions as an alkali agent in this recipe, as it is used in other dyeing recipes.
[16] Including cotton fabrics, which have a cellulose base, like wood.
[17] Original French: ""L'alum de plume est malaisé à piler, et ne passe poinct par le tamis. Par ainsy il le fault subtilier sur le mabre. […] Et celuy, blanc en pouldre, que vendent les apotiquaires est bon. Il se subtilie mieulx dans le mortier en pilant & trainant le pinon, ainsy tu le rendras fort subtil."
[18] For example, the fifteenth-century Bolognese Manuscript found in Merrifield's collection of recipes specifies "1/2 oz of alum ground very fine" in its recipe for arzica, and "roche alum in fine powder" for its recipe for a red lake. See Mary P. Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting* (New York: Dover Publications, 2003), 484, 432. Other examples of manuscripts citing a specific method for processing the alum include "ground alum" (from a recipe for Schutt gal, a yellow lake pigment, from a 1549 edition of the *Illuminierbuch*), and "crushed alum" (from a recipe for madder lake from MS cod. Pal. Germ 620, a fifteenth-century German manuscript), both foun in Kirby's *Natural Colorants for Dyeing and Lake Pigments* (82, 85). Other recipes for lakes largely mention "alum" or "roche alum" in a water solution (Kirby 82, 83).
[19] At the time of the sixteenth century, the author-practitioner would have likely had high quality alum available, as the process for extracting it from alunite had been refined and expanded to an industrial scale, with alum imported to France especially from Tolfa (Italy), and from Turkey. See: Cardon, *Natural Dyes: Sources, Tradition, Technology and Science,* 27. See also: Spike Bucklow, *The Alchemy of Paint*: *Art, Science and Secrets from the Middle Ages* (London: Marion Boyars, 2009), 27, 34.)

The author-practitioner is also familiar with the range of materials that could be classified as alum. At the time, several different substances could be classified as alum, but they were generally understood to be astringent substances, largely sulphates of iron and aluminum.[20] The author-practitioner is able to distinguish between the different kinds of alum, making reference to both stone alum and feather alum in his recipes for casting (fol. 107r). Stone alum, also known as roche alum, is a pure form of alum processed from alunite, the mineral form of hydrated aluminum potassium sulfate,[21] which yields the potassium alum most often found in dyeing and pigment-making.[22] Feather alum, by contrast, refers to a naturally-occurring crytalline ferric potassium sulphate alum now known as halotrichite.[23] Additionally, the author-practitioner makes reference to the characteristics of good stone alum, again showing that he can distinguish the quality of these materials for better use in his recipes: "Good stone alum is as white and as shiny as white silk, this stone alum Is made of long pieces, as long as a finger, and is very fragile and wooly and fluffy. Stone alum made of stone is harder and not so good. The best quality can be found in France near Ronan" (fol. 107r).

The author-practitioner's understanding of alum based on its uses and general characteristics rather than an exact chemical understanding of the process appears to be representative of recipe books from the seventeenth century, as the exact chemical nature of alum was not determined until the end of the eighteenth century.[24] Most contemporary recipes for lakes specifically mention the use of alum in the process of making lakes, but little details on the exact process—for example, the yellow lake recipes mentioned in in the Turquet de Mayerne manuscript (1620) describe a yellow of Avignon made from buckthorn berries "put in a solution of alum and water" and a yellow lake made from broom flowers and turmeric berries mixed with alum in a water solution with ceruse as a substrate.[25] In contrast, later sources from the 18th century like the *Traité de la peinture au pastel* start describing a general chemical process for making lakes.[26]

The author-practitioner's understanding of the role that alum plays in processes such as pigment-making is a very practical understanding—he is aware of alum's properties and makes use of it

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[20] Mary P. Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting* (New York: Dover Publications, 2003), xii. In modern-day terminology, alum can still be used to refer to a whole group of hydrated metal salts, with hydrated potassium sulfate most commonly referred to as alum.

[21]This compound has the chemical formula $FeAl_2(SO_4)_4 \cdot 22H_2O$. See: Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting,* xviii. See also: "Alunite," last modified 11 March 2016, http://www.mindat.org/min-161.html.

[22] This compound has the chemical formal $KAl(SO_4)_2 \cdot 12H_2O$, where the sulphate anion (SO_4^{2-}) is bonded to two cations: K^+ and Al^{3+}, surrounded by six water molecules. See: Ohrstrom, "Alum," *Royal Society of Chemistry.*

[23] This compound has the chemical formula formula $FeAl_2(SO_4)_4 \cdot 22H_2O$. See: Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting,* xii. See also: "Halotrichite," last modified 8 March 2016, http://www.mindat.org/min-1809.html.

[24] Ohrstrom, "Alum."

[25] See: Recipe 44, "Yellow of Avignon," and recipe 350 for dutch pink in *Lost Secrets of Flemish Painting*, Floyd: Alchemist Inc, 2001). See also: The yellow lake recipes mentioned in the Paduan manuscript of *Colori Diversi* simply mention buckthorn and saffron boiled in alum water, while another mentions burnt roche alum added to boiled buckthorn after boiling Found in Merrifield's *Medieval and Renaissance Treatises on the Arts of Painting*, 694.

[26]"In effect, if a certain quantity of alum is put is a concoction of dyeing plants, the ground of this salt leaves its acid and catches the principal dyes."
*Original French: "*En effet, si l'on met une certaine quantité d'alun dans une decoction de plantes colorantes, la terre de ce sel quitte son acide & saisit les principes colorans."
Paul-Romain Chaperon. *Traité de la peinture au pastel,* 82.

for a number of processes, and had a grasp of alum as a material for dyeing and making pigments. In this context, the omission of alum from the recipe for scudegrun in fol. 10r may have been a choice of phrasing on the part of the author-practitioner, rather than a mistake in the recipe—the author-practitioner seems to know enough about alum to identify that the lack of alum in this recipe would lead to the largely un-colored pigment that resulted from strictly following this recipe in the reconstruction. If it was a deliberate omission, it was likely not because alum would have been automatically understood as a necessary ingredient for a lake pigment recipe, as most other lake pigment recipes found in the process of researching this annotation do specifically mention alum.[27] Rather, the emphasis of its phrasing lies on the choice of ceruse or chalk as a substrate, rather than a description of the process by which this is achieved. The author-practitioner's intent for the 10v recipe for scudegrun may have been to act less as a recipe that stated the entire process of making the pigment and more as a suggestion of different substrates that could be used with a weld pigment for use with tempera or oil. The author-practitioner's purpose for this scudegrun recipe could be further informed by research into the opaque properties granted to a weld lake pigment by this choice of substrate were considered particularly desirable in sixteenth-century French painting practice, and whether ceruse and chalk produce different results as substrates.

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[27] See foonotes 20 and 27 for examples of alum mentioned in contemporary recipes.