Discovering Discovery: How Faraday Found the First Metallic Colloid

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In 1856, Michael Faraday (1791–1867) conducted nearly a year's worth of research on the optical properties of gold, in the course of which he discovered the first metallic colloids. Following our own discovery of hundreds of the specimens prepared by Faraday for this research, the present paper describes the cognitive role of these "epistemic artifacts" in the dynamics of Faraday's research practices. Analysis of the specimens, Faraday's Diary records, and replications of selected procedures (partly to replace missing kinds of specimens and partly to understand the "tacit knowledge" implicated in Faraday's research) are outlined, and a reconstruction of the events surrounding the initial discovery of metallic colloids is presented.

In an 1852 lecture before a general audience at the Royal Institution, Michael Faraday (1791–1867) demonstrated a fascinating property of metallic gold: In contrast to all other metals, "Gold has been beaten into leaves so fine as to become partially transparent,—not in consequence of any cracks, holes, or fissures, but by the shining of light through its substance" (Faraday 1853, p. 69). To illustrate his point, Faraday appears to have used a large gold leaf, about 3″ square, mounted on a glass plate 6″ square; the actual leaf still survives in the collections of the Royal Institu-

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Figure 1. [TOP] Faraday's large gold leaf. The leaf is 3″ square and is mounted on a 6″ square glass plate. Light from a fiber optic illuminator (off camera to the right) is partly reflected to the camera (the bright area on the right) and partly transmitted through the gold, to make the green shadow on the left. The illuminator is reflected from the glass plate at upper left.
[BOTTOM] Faraday's gold colloid (on the right of each pair) and a pink solution, made by Faraday to resemble a gold colloid (on the left of each pair). Note the similar appearance in ambient light (the pair on the left), but the scattering when light is transmitted through the colloid (the pair on the right). Courtesy of the Royal Institution. Photos by the author.

tion, and is shown in the top part of Figure 1. When light reflects off this gold leaf it has the familiar yellowish-gold appearance characteristic of metallic gold. But the leaf is thin enough to be transparent (ordinary commercial gold leaf was known by Faraday to be "One two hundred thousands of an inch in thickness"). Besides transparency, such leaf possesses another remarkable property: When light is passed through the gold leaf, "through its substance" as Faraday noted, it appears *green,* not yellowish-gold. The "shining of light through its substance" has changed the light.

Four years later, in 1856, Faraday spent most of the year in an attempt to explain these properties of gold. The major consequence of his work was the discovery of metallic *colloids* of gold and the characterization of their properties, including an optical effect known as the "Faraday-Tyndall Effect," later used by Tyndall to explain the light scattering implicated in the blue color of the sky.

In the present paper, I offer an explanation of Faraday's discovery of gold colloids, based in part upon a reconstruction of his experimental procedures. In earlier papers, my students and I have presented an analysis of the microstructure of his practices, specifically including attention to, and replication of, the *epistemic artifacts* made and used by Faraday. This work, and more recent replications described here, permit a cognitive reconstruction of Faraday's discovery processes (Tweney, 2002; Tweney, Mears, Gibby, Spitzmüller, & Sun, 2002; Tweney, Mears, & Spitzmüller, 2004). In the process, I will further justify attention to these epistemic artifacts used by Faraday, and to the "experimental ethnography" (Tweney, 2004) of our replications. Both artifacts and replications are essential components for a cognitive understanding of this important episode of scientific thinking.

By 1852, Faraday had made the major discoveries in electricity and magnetism for which he is best known—electromagnetic induction, the distinction between paramagnetic and diamagnetic substances, the rotation of a plane-polarized light beam in a magnetic field—and his field theory had been developed to its final form (see Cantor, Gooding, & James 1991). Over the next few years, Faraday continued to work on problems of electricity and magnetism, but he also was devoting a great deal of time to applied concerns (James 2000)—evaluating lighthouses for Trinity House, working on the problem of retardation in submerged telegraph cables, and engaging in the public debunking of psychics and mediums.

For a brief time, following the publication of the last of his major papers on electricity and magnetism, Faraday continued to work on an attempt to measure the time of propagation of a magnetic impulse (*Diary,* 19 January, 1856, §14238, p. 10).[1] Yet the research was frustrating, and the apparatus proved to be delicate and difficult. Within a few weeks, Faraday dropped the problem in favor of an extensive attempt to explain the optical properties of gold. In a letter to his friend, the German chemist Christian Friedrich Schönbein (1799–1869), Faraday noted that "I have been occupying myself with gold this summer; I did not feel headstrong enough for stronger things—The work has been of the mountain and mouse fashion; and if I ever publish it and it comes to your sight, I dare say you will think so:—the transparency of gold—its division—its action on light." (Faraday to Schönbein, 14 October 1856, in Kahlbaum & Darbishire 1899, p. 274).

In the end, the "mouse" brought forth by Faraday's "mountain" of research was more consequential than he had anticipated (Faraday 1857). The recognition that gold metal could form "colloidal" suspensions of particulate matter proved to be a landmark in the history of colloid chemistry.[2] Further, his systematic exploration of the optical properties of gold in its various states—especially as thin transparent leaves, and as colloidal suspensions of very fine submicroscopic particles, was important for the understanding of metals in general. In the end, there was a continuity between the problem of "the transparency of gold—its division—its action on light . . . " and his views on the nature of electric and magnetic fields and of their interaction with matter. Gold was a good problem precisely because it held the promise of clarifying the close interaction of light and matter.

Cognitive Science and the Understanding of Faraday's Gold

One issue for cognitive science concerns the way in which the larger "Purposes" of a scientific career come to be instantiated in specific programs of research. Previously, I argued that such purposes constitute the "slow waves" of change across years and decades (Tweney 2001). For example, Faraday's discovery in August 1831 of electromagnetic induction had roots in his research, earlier in 1831, on optical illusions of motion and on

1. In the present paper, all references are to Volume 7 of the published edition of the *Diary* (Martin 1936).

2. Faraday did not use the term "colloid," which was coined by Thomas Graham (1805–1869) in 1861. My use of the term here is purely for convenience of reference; Faraday himself usually referred only to the "ruby fluid" or "violet fluid," coding the color of the preparation but without ontological implications. On Faraday's careful use of lexical terms to refer to specific entities and processes, see Anderson (this issue) and Tweney (1991). As noted below, Faraday's failure to coin a specific term may be related to the uncertainty that he felt over the outcomes of his research.

the vibrating surfaces of fluids (cf. Cavicchi, this issue; Gooding, this issue; Ippolito & Tweney 1995; Tweney 1992).[3] "Faraday's Gold" represents another case in which such slow dynamics are implicated in the dynamics of laboratory practices. In this instance, we can trace the manifestations of his field-like notions of electricity and magnetism and his earlier speculations about a possible ether (Faraday, 1851) into his novel account of the nature of matter-light interactions. As for the "fast" dynamics, the focus of the present paper, these became visible partly through a remarkable group of surviving specimens used by Faraday, and partly by being *made* visible through replication (Tweney 2002).

In the research on gold, Faraday used experimentation and a set of constructed epistemic artifacts as critical exploratory tools to construct a theory of the interaction of light and matter. Characteristically, Faraday's theory construction was modulated by a series of dynamic laboratory practices and by interaction with the physical domain of artifacts used in his research (Cavicchi 2003; Gooding 1990; Steinle 2002). In the present case these interactions can be tracked across an entire program of research lasting almost a year, during which he conducted hundreds of individual experiments and prepared over a thousand specimens. The unique value of the present case resides in the rich body of evidence available in the form of the specific specimens used by Faraday during the research.

Some cognitive models of scientific thinking have emphasized the role of search through a problem space as a core activity of science (e.g., Kulkarni & Simon 1990; Schunn & Klahr 1996; Tweney & Hoffner 1987). Such models have come under criticism, however, on the grounds that they render the cognition of the scientist irretrievably locked in a space of symbols "within the skull"; such a view makes it difficult to understand the role of cognitive artifacts or the social environment within which science proceeds. Thus, Greeno (1994) argued that studies of thinking must emphasize the important participation of the affordances of the environmental objects and the "abilities," (the attunements to constraints) within which thinking occurs. Similarly, Nersessian (2004, see also Kurz-Milcke, Nersessian, & Newstetter 2004) has emphasized the importance of the interactions among cognitive agents and the environment of cognition for the understanding of science especially. Accounts that are limited

3. Frank James and David Gooding replicated some of Faraday's illusions during a talk in July, 2003 at the Royal Institution and were able to enhance them by using video cameras and a strobe light (Gooding, personal communication). Faraday had no strobe light, of course; instead, his procedure for "stopping time" relied upon experimental inference, construction of mental and physical models, and a close geometric analysis of the dynamics of apparent motion (Cavicchhi, this issue, and Tweney 1992).

to only the representations and goals of scientists will thus be incomplete at best and misleading at worst.

Much recent work in the history of science and social studies of science has emphasized the close analysis of laboratory practices (e.g., Gooding, Pinch, & Schaffer 1989; Holmes, Renn, & Rheinberger 2003). These are more closely related to recent cognitive anthropological approaches, rather than to the problem space approach (see, e.g. Atran 2002; Hutchins 1995). In the end, both approaches may be needed. Thus, Kurz (1998), in an analysis of the mathematical "problem finding" activities of mathematicians and scientists, suggested that problem space search is a component of the *late* stages of some scientific thought, after relatively stable representations are available. Problem space search is less useful as a model of how representations are formed in the first place; here a cognitive ethnographic approach is more promising. Even so, to be fruitful, an ethnographic approach must be able to accommodate a rich level of detail, down to the smallest level of observable texture. In this respect, the present case represents a nearly unique opportunity.

"Faraday's gold," as I present it here, is an instance of an *experimental* cognitive ethnography (Tweney 2004; see also Cavicchi 1997, Gooding 1989, Heering 1989, and the papers in Heintz 2004). Our development of the case depended upon a series of replications of the procedures used by Faraday. The goal of the replications was to recreate specimens that no longer exist and, more importantly, to reconstruct the cognitive dynamics of the growing and changing representations of phenomena, tracking these changes through the *Diary.* In this respect, replications are a manifestation of a particularly intense "reading" of the Diary text. Similarly, Lawrence Principe (1998) used replication as a tool to establish new readings of alchemical works, showing that they are coded presentations of actual chemical procedures, rather than allegorical or "merely" symbolic texts. I begin by describing the surviving epistemic artifacts made by Faraday himself—these provided the rich "ethnographic" materials that initiated the cognitive account.

The Epistemic Artifacts

Several years ago, I made an unexpected discovery: The museum area of the Royal Institution where Faraday had lived and worked held a group of boxes containing more than 700 surviving microscope slides and other specimens made by Faraday as part of the 1856 research. Most of the specimens were gold films mounted or deposited directly on ordinary 1″ x 3″ glass microscope slides. The slides were numbered in Faraday's hand, and the numbers on the slides corresponded to the numbers indexed and referenced in his Diary for 1856. Examination of the slides revealed that they

Figure 2. Some of the boxes containing Faraday's slide specimens. Courtesy of the Royal Institution. Photo by the author.

constituted nearly the complete set of metallic film specimens used by Faraday in 1856, and many other specimens as well. The slides had been "hidden in plain sight," in an area in which Faraday's "magnetic laboratory" had been reconstructed for public display, visible only through a ceiling-height Plexiglas barrier. They had been overlooked for many years because they were part of a diorama, visible but untouchable by scholars and the public (Tweney 2002).

It had long been known that some of Faraday's gold colloids survive from the 1856 research: Four bottles of these are on display at the Royal Institution in London (See Figure 1, bottom). They contain very pale blue or gray fluids and show a clear Faraday-Tyndall Effect. That is, if a narrow beam of light is passed through the colloid, the light is scattered sideways, rather like a sunbeam through smoky air.[4] These few colloids are all that survive of many dozens referred to in the Diary. It is no surprise that most have not survived—part of what Faraday established in his research were the conditions under which colloids are stable or unstable, in the course of

4. A fifth bottle contains a pink fluid and has long been taken as the "best" of the colloids, but it does not show the Faraday-Tyndall Effect, and must therefore be a solution, not a colloid.

which he made many that were unstable, and destroyed many others as he explored the conditions of stability.

By contrast, the surviving gold film specimens, the nearly 700 microscope slides, are the nearly complete set of these important specimens. They "fill in" a critical missing dimension of the *Diary* especially since *Diary* descriptions of the slides are brief and sometimes cryptic. Thus, while the text of Faraday's *Diary* is known for its generally amazing completeness (Tweney 1991), in this part (from February to December of 1856) we can now see that the *Diary* was intended to include the specimens. Faraday was careful to number and cross-reference the specimens, to coordinate the numbers across different types of specimens (e.g., colloids were Roman-numbered, while slides were numbered with Arabic numbers), and to construct boxes with numbered slots to hold the slides (Figure 2). As a result, the *Diary* text and the slides together constitute a kind of "super-*Diary.*"

Why should a scientist wish to save such specimens? This seems like an obvious question with an obvious answer—to preserve a record of lab activity and to preserve evidence. But asking the question opens up other, less obvious, issues. First, as Gooding (1989) noted, the private records of a scientist are always incomplete, partly because of gaps in the record and partly because of the "tacit knowledge" of the experimenter. Gooding criticized the exclusive preoccupation with only the *texts* of science and used his own replications of Faraday's 1821 experiments on electrical rotations to enhance Faraday's diary record.

Besides "gap filling," a deep understanding of a diary record requires attention to the specific practices and phenomena which are represented. Gooding's replications of Faraday's 1821 experiments involved suspending a magnetic needle near a current-carrying wire. He observed that the motions were nearly chaotic in appearance, showing orderly appearances only when successively constrained by continual refining of method and apparatus. Faraday's "space" of *practices,* not just his diary record, was required to understand the discovery. In the present case, Faraday's slides must also be part of the "space" of Faraday's discovery processes. Certainly the slides were consulted during preparation of his lectures and papers, just as the *Diary* was consulted, and as part of the same whole. But the slides were more than *mere* records, as I show. Thus, an account based solely on the mental constructs, the symbolic "space," that Faraday brought to bear on the understanding of gold would be inadequate, for the simple reason that the specimens themselves constituted agents in the discovery process; the properties and behavior of the slides themselves acted to change the developing knowledge representations. The slides were *epistemic artifacts,* parts of a cognitive *system* which produced the knowledge arising from the research. (Tweney 2002; see also Rheinberger 1997). Thus, one reason for Faraday to save the slides was to enable repeated interaction with these agentive entities. In effect, preserving the specimens allowed him to re-question them in the light of later specimens and in the context of his evolving understanding.

Establishing the Cognitive Questions: Initiating the Research on Gold

In his first *Diary* entry on gold, Faraday noted that he began his research on January 28 of 1856 by visiting his friend Warren De la Rue (1815–1889): "Wishing to look at Gold leaf in a good Microscope, I applied to Mr. W. de la Rue, and he has undertaken to aid me with his instrument" (*Diary,* 2 February, 1856, §14243, p. 11). Faraday described the appearances they had observed, and noted that De la Rue sent him, on February 1, some specimens of thin films of gold attached to glass plates, films made by a chemical technique (De la Rue was engaged at the time in research on better ways to coat telescope mirrors with silver and gold). As opposed to the mechanical hammering operations used to make commercial gold leaf, these chemical films were much thinner; "They are beautifully thin. Yet when examined by a microscope of high power, they appear to be perfectly continuous and uniform" (*Diary,* 2 February, 1856, §14257, p. 13).[5] Further, most of these thinner films appeared *blue* by transmitted light, rather than the more commonly seen *green* color of commercial gold leaf. This further extended the question of just why gold can manifest so many different colors.

Faraday's first systematic exploration involved a close comparison of the color of the gold films and the color of the more familiar precipitates of gold (*Diary,* 5 February, 1856, §14291 etc., p. 18). None of his precipitate specimens survived, of course—they would simply dry and harden over time, irreversibly losing their character.[6] This was the first clear instance where we needed to replicate some of Faraday's specimens, ones that would not otherwise have been available (Tweney, Mears, Gibby, Spitzmüller, & Sun 2002). At first, we were encouraged by what struck us as

5. Faraday had no way to measure the thickness of the chemical films directly, but they can be made in a variety of thicknesses (by varying the time of the reaction), and they are clearly thinner than commercial leaf.

6. By present-day understanding, *solutions* consist of particles of atomic size, ions, carrying an electrical charge and dispersed through a water medium. *Precipitates* are formed when the charges on ionic particles of a substance are neutralized, thus allowing aggregation into large insoluble particles. Ions are much smaller than the particles that constitute precipitates, and they affect light in different ways. Precipitates are dense, cloudy, suspensions that settle more or less rapidly, whereas solutions are clear and transparent, no particles of any sort being visible.

the chemical simplicity of the procedures; just add a little ferrous sulphate to a gold chloride solution, and you should have a precipitate. Yet the simplicity of Faraday's description (*Diary,* 5 February 1856, §14291–14293, pp. 18–21) masked an underlying complexity that we did not appreciate until we tried the procedures. In effect, there are many "gold chlorides," including AuCl, $AuCl_3$, and a variety of hydrolyzed species of each of these. Each variety differs in crystal structure, stability, color, and solubility, and we wasted a good deal of time in trying to find the right commercial product that could simply be dissolved in water.[7] Unfortunately, Faraday mentioned only that his gold chlorides were prepared by dissolving gold in Aqua Regia. For him, the complexity of these salts was a matter of laboratory *practice* (in his *Chemical Manipulation* 1827, Faraday devoted an entire chapter to techniques for producing solutions). In the end, we followed suit, dissolving a sample of pure gold in Aqua Regia (a mixture of hydrochloric and nitric acids) and boiling the resulting solution at constant volume to drive out the residual nitrogen oxides (Tweney, et al. 2002).

The basic procedures needed to prepare the precipitates, including the apparatus, were ones that have not changed in the many decades between Faraday's time and our own; many of them predate Faraday's time. The technologies of dissolving salts and mixing acids to make Aqua Regia rely upon beakers and flasks very like Faraday's, although it is interesting to note that the common test tube was used first by Faraday (Jensen 1981). We did use a modern hot-plate and magnetic stirrer to facilitate solution processes, but these represent conveniences, not essential changes. In this sense, it could be said that they displace a need for certain kinds of laborious practice (e.g., stirring a solution while it dissolves). In fact, a certain amount of "craft skill" is involved , even in so simple a matter as stirring a solution. Thus, Faraday's (1827) book, *Chemical Manipulation,* deals specifically with the operations of stirring, and he even, between the first edition of 1827 and the second of 1830, changed the section slightly to acknowledge a trick mentioned by his friend Richard Phillips, who advised heating the glass stirring rods in their center and thus bending them slightly, in order to prevent them from rolling around on the bench top. We did use glass stirring rods (unbent, and they *do* roll around!) for occasional stirring tasks, relying upon the hot plate and magnetic stirrer only

7. In solution, the ion is apparently not Au^- or Au^{---}, but instead generally exists as an $AuCl_4^{----}$ ion, again with a variety of hydrolyzed species. None of this was clear in 1856, although there was recognition that gold chlorides were complex and confusing chemically. See Brande (1836) for a contemporary account and Puddephat (1986) for a modern one.

for those times when extended stirring was needed. Note that changing these practices does not change the conceptualization of the reactions that result; the stirrer and the hot plate are not themselves cognitive agents. Similarly, Faraday's heating device (actually, a rather "high tech" sand bath) was not a cognitive artifact, nor can we regard his labor as "stirrer" to be an epistemic activity. Making a solution does not, of itself, add to knowledge.

By contrast, the procedure of comparing the color of the precipitates to the color of gold film *was* epistemic. Consider the beginning of the *Diary* record, before Faraday had done any more than simply visit De la Rue. In this beginning section, Faraday laid out some of the major goals of his research and some of the procedures he was considering. He was hoping to find evidence for the *continuity* of thin gold films, as opposed to the idea that they could represent discontinuous, or *particulate* matter. The possibility required careful attention to how the colors were produced. Faraday wrote:

> 14278. If a wedge film [i.e., a film varying in thickness from one end to the other] obtained by chemical action or by electrical action proceeds in the different parts from the first tints to green—and superposed plates do not—that will shew that there is cohesion of parts and continuity in the first plate and not merely a layer of fine particles.
>
> 14279. Gold precipitated by sul. iron gives I think screens of different colours at different times. If this is not due to addition of the effect of the persulphate of iron produced, it is probably due to the different sizes of the particles. As these particles are probably less in thickness than the thickness of a transparent plate of gold, they ought to transmit coloured light; and as they are separate the one from the other, the light through a greater number of them ought not to be changed in colour though it should be diminished in quantity.
>
> 14280. Let a precipitate settle: does the colour of the column then vary in different parts, as particles of different sizes arrange themselves at different depths. Use a rectangular column so as to compare width in one direction with breadth in another part and direction. (*Diary,* February 5, 1856, p. 16).

Faraday then varied systematically the thickness of the films—"a wedge film . . . [vs.] superposed plates"—and of the dimensions of precipitated particles—"Let a precipitate settle . . ." He thus set up a direct comparison of the color of precipitates to that of films, in the context of trying to analogize one set of variations, that of film thickness, to another set of variations, that of particle size and number as established by settling time. This procedure is epistemic because it speaks to the issue of whether or not gold films are continuous, and to whether the color of precipitates can be explained as an aggregate result from the color of individual particles. That is, if the precipitates show similar changes in color, then perhaps films are also particulate.

There is a close coordination here between theory and empirical practice. Faraday was using a complex heuristic, one in which analogized relations were carried over from one domain (precipitates) to another (wedge films and “stepped” films). Since each domain was only partly understood, this amounted to a kind of “bootstrapping” in which analogy was used to bring two incompletely understood domains into one hopefully better understood domain. Clearly, this heuristic does not amount to a proof procedure. Further, Faraday’s extensive use of such complex heuristics implied a convergence among a multiplicity of experiments and procedures (Cavicchi, this issue; Gooding 1990). Such strategies are the roots of his characteristic style of research.[8]

The distinctions I am proposing, between epistemic and non-epistemic artifacts and procedures, can thus be established for the Faraday gold research, supporting and extending previous cognitive characterizations. In the following section, I show that the epistemic artifacts were used in both an exploratory and an explanatory manner, and that their existence can help to explain the discovery of colloids.

Explaining the Discovery: Recognition, Reorganization, and Categorization

According to present-day understandings, a colloid consists of finely divided particles of a substance, like precipitates, except that the particles are smaller in a colloid (and colloids do not settle, whereas precipitates do). By contrast, colloids differ from solutions in that the particles are far larger than the ionic particles of a solution (and neither settles out). Like solutions, metallic colloids are clear and transparent—the particles are not visible. Solutions of gold chloride are clear and yellow-gold, whereas gold colloids are clear and range in color from pale pink, through ruby red, to a blue or purple color. And since colloids do not settle, it would be easy to presume that they were like solutions, not precipitates.

8. Note that most descriptions of the use of analogy in science have emphasized its role in bridging a better-understood domain to a lesser-understood domain, rather than, as here, its role in bridging two poorly understood domains (e.g., Dunbar 1995; Nersessian 1999). Similar heuristics also were relevant to characterizing Faraday’s style of exploratory research (Steinle 2002; see also Burian 1997).

Faraday noticed “ruby fluids” (i.e., what we now call colloids) very early in the course of the research, during a second visit to De la Rue on February 6, 1856. This is the event that we now regard as “the” discovery of metallic colloids. Why did he notice them? Why at that moment? Having noticed them, how did he recognize the need for a reorganization and how did he use this reorganization as the basis for a new categorization? These constitute the major *cognitive* questions of the present paper.

Note first that we cannot see the incident as a case in which Faraday used a logical extrapolation, nor did he predict the existence of the new substances from previous results. The existing scientific context was simply not sufficient to “prime” such noticing.[9] Metallic colloids were *not* inferred from the existence of other known colloids, nor was their existence predicted. Thus, while Thomas Graham was by 1856 well on his way to characterizing the nature of colloids in general, his work was almost entirely with organic colloids, whose character was very different from those Faraday encountered, and neither Graham nor Faraday cited the other’s work. Instead, the clue to explaining Faraday’s discovery resides in an emergent recognition and a subsequent conceptual reorganization.

In the next section, I first describe the reorganization, which *followed* his first recognition of the ruby fluid. This will then permit us to see the reasons for the noticing itself. As will be clear, our understanding of both the noticing and the reorganization required that we conduct replications in order to make visible the cognitive agencies involved. We also had to recognize, reorganize, and categorize.

Conceptual Reorganization

Consider first the way Faraday worked during his first observations in his own laboratory (5th of February, 1856) following his first visit to De la Rue. Since gold in a continuous state changes appearance in transmitted light and reflected light, he first developed an “optical method” for examining the films in both kinds of light. Faraday next compared thin films (which he suspected to be gold in a *continuous* state) to precipitates, which he knew to be *discrete particles.* He thus compared light *passing through* and *reflected from* both gold leaf and gold precipitates.[10]

9. It is interesting to note that in 1827 Faraday described a suspension of animal charcoal in alcohol (probably what we would call a colloid) as a means of determining the direction of light by “a degree of opalescence” in the fluid (Faraday 1827, p. 585). This passage was removed from later editions of the book, and there is no indication that he ever relied upon this observation in his work on gold.

10. Frank James (1985) first examined the extensive use made by Faraday of the “optical mode of investigation,” some examples of which were described in Faraday’s *Chemical Manipulation* (1827, pp. 585–586). See also Chen (2000), who argued that, for some scien-

The next morning, the 6th, he again visited De la Rue in order to learn about his method of making thin films of gold using a phosphorous reduction technique. Once made, the films were floated onto the surface of a bowl of water in order to clean them, then mounted on microscope slides for later examination (*Diary,* 6 February, 1856, §14319, p. 21). Most notably, Faraday recorded a seemingly incidental observation of the water used to clean the slides: "A very fine red fluid is obtained [from] the mere washing" (Diary, #14321, p. 22). Incidental or not, Faraday saved the fluid, returning to it two weeks later on the 18th. He was then able to ask of this red fluid; " . . . the question is, is it [i.e., the gold] in the same state as whilst apparently *dissolved* in the fluid" (§14437, p. 43, emphasis in original). Interestingly, in his initial entries, Faraday referred to the red fluid using two terms interchangeably, "fluid" and "solution". Only later, when he was he sure that the red fluid was *not* a solution, did he become consistent in referring to the *fluids.* This terminological shift signals the reorganization that we must understand.

As we have seen, preparing precipitates was the first activity undertaken by Faraday, on February 5th. He must therefore have had before him the *clear* solution of gold chloride, that is, the gold dissolved in Aqua Regia. At De la Rue's, the next morning, he explicitly noticed the *clear* red solution that was a byproduct of the reduction technique, "the mere washing." He knew that the substances used to produce the clear red solution (phosphorous, carbon disulfide, and a gold chloride solution) produced metallic gold. But why then did the byproduct look like a *solution?* If all the gold had been released in the pure metallic state (as a film) by the phosphorous, the only possibilities for solutions involved sulfur, phosphorous, and chlorine—and none of these was known to produce a solution in this context.

On the 8th, two days after his second visit to De la Rue, he recorded an observation:

> The red fluid (14321) made 6 Feby. does not apparently settle; is uniformly red. A portion passed thrgh. a filter twice went through red, but also left a stain on the filter shewing the separation of some of the particles. (*Diary,* February 8, 1856, §14342, p. 25).

This (and several other observations) suggested that the fluid was at least partly particulate. When he poured off a sample and let it sit, a thin film of gold slowly formed on the surface and a lumpy precipitate of gold ap-

tists of this era, as for Faraday, the eye was itself regarded as an optical instrument in the context of experiment.

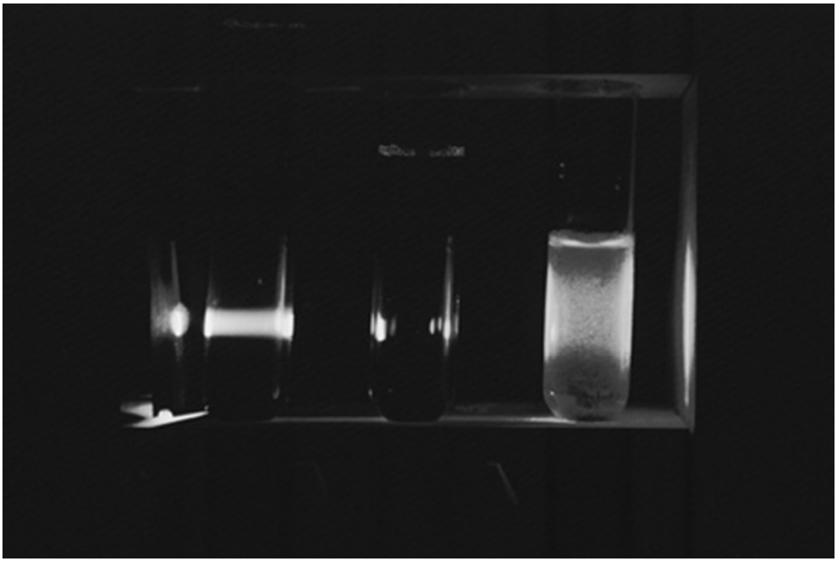

Figure 3. Our replicated colloid, solution, and precipitate (from left to right). Note that the colloid and the precipitate both scatter the light beam (entering from the left). Photo by the author.

peared at the bottom of the dish. This also suggested that the red fluid was a particulate suspension *of gold,* rather than of some other substance.

The first clue about Faraday's "noticing" came to us during our first replication efforts. We had prepared a gold colloid (using modern methods, unlike Faraday's but with similar results; see Tweney et al. 2002), and we had begun to subject our preparations to "optical modes of investigation." We used three of our preparations, a gold colloid, a gold solution, and a gold precipitate The three preparations showed the expected appearance in ambient (room) light; the solution was a clear, deep yellow fluid, the colloid was a clear ruby-red fluid, and the precipitate, when shaken, was a cloudy yellow-gold suspension in which individual particles could be seen in motion, and in which occasional glints of bright metallic gold could be seen. Except for the overall color, the solution and the colloid appeared to be very similar—clear and transparent—while the shaken precipitate had a very different appearance—cloudy and opaque.

The relative similarity of the three changed, however, when directional lighting was passed through the fluids (Faraday had used a mirror and a blackened tube to direct a single beam of sunlight through his specimens). Figure 3 shows the effect of a parallel beam of light produced by a fiber-optic illuminator (entering from the left) on our prepared gold colloid, a solution of gold chloride, and the precipitated gold preparation, respectively. Note that the colloid shows a bright "Faraday-Tyndall Effect," that is, light is scattered to the side, illuminating the path of the beam through the colloid. A similar scattering is visible in the precipitate. Obviously the colloid and the precipitate resemble each other most closely under these optical conditions, in contrast to the appearances in ambient light.

There is no record in the diary of Faraday placing all three of these substances in one context (as we have done in Figure 3). Yet it is clear that he was attending these differences very carefully—in his published paper, they constituted part of the rationale for his conclusion that the ruby fluids were suspended particles of gold (Faraday, 1857). Yet only weeks after the first noticing did Faraday *record* the use of transmitted light with a ruby fluid and hence "the" discovery of the Faraday-Tyndall Effect (*Diary,* February 27, 1856, §14453, p. 46), after which he conducted a number of experiments on the composition and stability of the fluids. Apparently he was on the track of the particulate nature of the ruby fluid from the beginning, but simply had an "embarrassment of riches" by way of possible experiments. Thus, by the 27th, when he finally recorded using both transmitted and reflected light on a ruby fluid, the procedure was presented as a routine one, and no special comment was made—in fact a novel and extremely important maneuver had been carried out!

Initially, then, Faraday used *both* transmitted and ambient light with the precipitates and the gold leaves. As noted, his theoretical predisposition was to find a way to distinguish between matter in a continuous state and a discontinuous (particulate) state. Precipitates are obviously particulate and the thin gold films *could be* continuous. But if so, there was a need to prove that continuity, and the initial comparisons must have been frustrating—precipitates scatter light, but the scattered light mostly just looks either yellowish or has flecks of metallic shiny gold visible in it. There is nothing resembling the dramatic change in color that a gold film provides when light is transmitted through it. By contrast, transmitted light made his ruby fluid look very different from the clear solution. A reorganization became necessary—the "red fluid" must be gold in a "divisible state," like the precipitates and unlike the solutions.

Noticing the Ruby Fluids: "The" Discovery

We must now return to the main issue—*Why* did Faraday notice the ruby fluid on February 6th in the first place? The answer resides in the nature of the procedure used to make the thin gold films. The procedure which De la Rue showed Faraday that day is chemically simple:

> Evening. Have been this morning to De la Rue's to learn his mode of making the films of Gold—is as follows. A piece of phosphorus . . . is dissolved in . . . Sulphuret of carbon . . . —a solution of Gold free from acid and containing about a sovereign in 2 or 3 ounce volumes forms the second fluid G. A clean plate of flat glass about 5 inches square . . . a large Wedgewood's dish holding 3 or 4 quarts of water . . . . A little of the phosphorus solution P was poured into the glass capsule and moved over its surface to distribute the phosphorus—most of the sulphuret of carbon evaporated. A portion of the gold solution G was poured on to the *clean* glass plate—spread over its surface by a glass rod . . . , and then the wetted plate inverted and placed over the phosphorus in its capsule; gradually a film of gold formed which could be recognized by reflected light because of its colour and appearance. Then the glass plate was turned up and, being brought over the dish of water, was inclined a little to the horizon and depressed until one edge and gradually the whole was under water—the metallic film floats . . . . A piece of glass or of card being immersed in the water—brought beneath the film and raised, brings up the film with it . . . . (*Diary* February 6, 1856, §14319, pp. 21–22).

We had little difficulty in replicating these procedures, and in the process gained insight into what might have been especially "noticeable" to Faraday.[11] Phosphorous is highly soluble in CS_2, so this part of the procedure was straightforward. And, once we had placed the solution in a watch glass (his "capsule") and covered it with a glass plate, it became apparent that the small amount of air above the solution was soon consumed by oxidation, and the result was a phosphorous-vapor impregnated atmosphere. We then "filmed" the bottom of a Petri dish (corresponding to his "glass plate") with the gold solution and inverted it over the watch glass (we soon found that the bottom of the Petri dish had to be *exceptionally* clean, as he noted, in order for surface tension to hold the gold chloride to the dish in a uniform thin layer). Within 5 minutes or so, a blue fringe could be seen around the edges of the gold solution: a reaction was occurring.

11. Actually, only the chemistry itself proved unproblematic. The practical difficulties of obtaining and using the required materials were very great, especially given the need to conform to modern standards of health, safety, and disposal. We are Indebted to Lawrence Principe for his invaluable assistance in navigating these constraints.

Figure 4. A "gold film by phosphorous," floating on the surface of water. Photo by the author.

When we inverted the Petri dish and slipped it gently into a bowl of water, we found a very visible (and very thin!) gold film floating on the surface. This was then lifted onto a glass slide and dried for examination (Figure 4). Perhaps the most surprising aspect of this procedure is its simplicity. In several different attempts, we had no difficulty in getting the films to form. And the appearance of our slides was very similar to his, even under high magnification.

The most telling finding came about unexpectedly. In our first trials with the gold films, we used a dark metallic bowl as a container in which to wash the films. Later, we switched to a white ceramic bowl in order to better photograph the floating films. After a few hours of work, we noticed that the water in the bowl, "the mere washing," had turned a very pale pink. This was the "ruby red fluid," which we saved into a clear jar. The fluid manifested a prominent dispersion cone when a beam of light was sent through it. While it darkened to a violet color after a few days, even months later, it remained clear and continued to disperse light. The appearance of this fluid made it clear that Faraday had noticed a phenomenon that was hard to miss under the right circumstances; in particular, the "washing bowl" had to be light in color!

Thus, while initially Faraday was prepared to compare the various colors of gold films and gold precipitates, the newly noticed "ruby fluids" had to be included as well. Metallic gold was implicated in all three and it was notable that the range of the colors of gold that had impressed Faraday was now even wider—within a few days of beginning his research, he had come to see that more than just the difference between transmitted and reflected color was at stake. For Faraday, as for me and my collaborators, a sequence of puzzling analogies was at play, and these had to be, first, recognized as important, second, used to create a new organization, and, third, used to re-categorize the substances involved. The ruby fluids were particulate, like precipitates, and the analogous appearance of the fluids and the films under transmitted and reflected light carried the strong implication that the gold films were particulate also.

From Discovery to Proof

Over the next several months, Faraday sought to prove that the ruby fluids were "divisible gold," and to ascertain their properties. Most importantly, he sought to understand their relation to the colors of thin gold films.[12] The strategy followed by Faraday over the next several months represented a kind of "spiraling" of the network of enterprise, one in which the evolution of his ideas about gold was manifested by a successive return to similar questions and methods, with, over time, a gradual deepening of his understanding of the phenomena. In the laboratory, therefore, it is no surprise to see that he alternated between the films and the colloids, working first with one, than the other. The process resembled one emphasized by Gruber (1974) in his analysis of Darwin's gradual development of the theory of evolution by natural selection.[13]

In the end, Faraday concluded that all the evidence pointed to effects due to particles of gold. Further, he argued that the colors produced by the particles of gold in a thin film must depend for their appearance upon the

12. One of his best clues came from "exploding" gold wires using rapid electric currents. We described these experiments and our replications in Tweney, Mears, & Spitzmüller 2005.

13. Gruber argued that the diversity of Darwin's "network of enterprise" provided opportunities for "chancy interactions" to occur, and that these were the ground for his insights.

Figure 5. One of Faraday's gold films (#206, on the left), and one of our replicated gold films (on the right). The physical appearance and color (a pale bluish-gray) is similar, although our film is thinner (in this instance) than Faraday's. Courtesy of the Royal Institution. Photo by the author.

interaction of light with *arrays* of particles. Color was something that happened *among* sets of particles, and was not the result of adding up the color of individual particles themselves; "The particles seem to form the equivalent of a continuous plate of transparent substance. . . . Their association is such as to present as it were an optical continuity" (1857, pp. 438–439). This was a true "field-like" conclusion, in its own way a stunning extension of his field theory to the nature of matter and the nature of light, yet qualified by "as it were."

In the published version of his results, Faraday expressed some diffidence. He placed his results (perhaps sarcastically?) in the context of "That wonderful production of the human mind, the undulatory theory of light . . . " (1857, p. 391). Yet the results were not definitive, and certainly not as a test of the wave theory, nor any other; "I do not pretend that they [i.e., the results] are of great value in their present state, but they are very suggestive, and they may save much trouble to any experimentalist inclined to pursue and extend this line of investigation" (p. 393). Faraday's tentativeness probably also explains his failure to seek a terminological anchor for the "ruby fluids." He was not ready to accord them ontological status, nor did he regard his discovery as ready for movement toward a consensus among scientists concerning a new concept (Caneva 2002). In the end, it was Thomas Graham, not Faraday, who named colloids, but in a very different context, one not seen as relevant to Faraday's "ruby fluids" until much later.

Conclusions and Implications

The specimens, those found that were prepared by Faraday, and those replicated in our lab, enhanced the cognitive record, which is distributed across artifacts, text, and the inferred mental representations of Faraday. When lost specimens (which included all of his precipitates and most of his colloids) were restored, then the record became complete enough to permit seeing aspects of the cognitive arena of Faraday's research that were otherwise hidden. In the end, this enabled reconstruction of the path of discovery. The replications led us to understand the path to his recognition of the significance of the ruby fluids, and his eventual conclusions about the field effects of matter. Just as Faraday needed specimens of gold to understand the nature of gold, so also did we need to prepare specimens of gold to understand the nature of Faraday's epistemic practices. Our exploratory experimentation could thus be seen as similar Faraday's (Steinle 2002), although our "object" was not gold but Faraday.

To account for the investigative pathway of Faraday's research on gold, it was necessary to elaborate the microstructure of that pathway. As Holmes (2004) noted, this is obviously not possible for every case, nor would that even be desirable. But when it is done for some cases, these can shed light on the processes that may be implicated in others as well. The "context of discovery" does have discoverable characteristics. To make such generalization possible depends, of course, upon there being a consensus that the processes observed in one study, however rich in detailed analysis, are in fact more than simply the contingent manifestations of a unique case. How do we know, as Burian (2001) has noted, that the case is not simply the result of a casting about for just and only the observations that support a preconceived notion? Or, to put this in Kuhnian terms, if a case based analysis of a scientific project depends upon contingent circumstances, how can we know that there is any commensurability with any other case analysis? For Burian, the key is to look for trans-theoretical and trans-disciplinary means of achieving agreement. Such agreement actually happens in scientific research, even in the most exploratory kinds, and explication of such situations opens to view the constraints that must be satisfied to achieve it. In the end, these constraints serve also to constrain the historian's analysis.

An experimental cognitive ethnography similarly provides for the constraints on analysis that are needed (Kurz-Milcke, Nersessian, & Newstetter 2004). In effect, the method returns Faraday to the natural world that he himself was studying. He becomes, for analysis, a cognitive agent within the world of his laboratory, not simply an inferred and disembodied "mind" known only through his texts. In this sense, case studies like the present one contribute to a richer view of the scientific enterprise, both past and present.

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