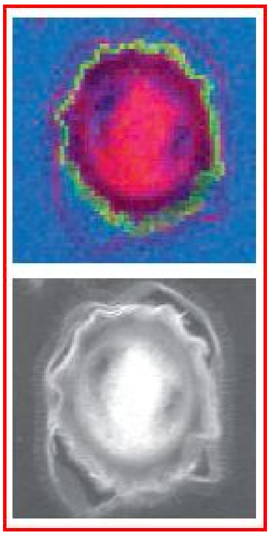
DETAILS OF SILICON-TIN CHEMISTRY OF ANTHRAX ATTACK SPORES PUBLISHED; WILLMAN TUT-TUTS



Sandia National Laboratories image of attack spore. In the upper frame, silicon, in green, is found exclusively on the spore coat and not on the exosporium (outer pink border).

On Saturday, the *Journal of Bioterrorism & Biodefense* published an article (pdf) by Hugh-Jones, Rosenberg and Jacobsen that provides the details of their theory, first described in a McClatchy article, that the anthrax spores employed in the 2001 anthrax attacks were "weaponized" by a process that involved tin-catalyzed polymerization of silicon monomers. Wasting no time, David Willman was quickly trotted out in the Los Angeles Times on Sunday to tut-tut this latest information as arising from “critics” of the FBI and to provide an outlet for those who unquestioningly parrot the FBI’s conclusion from its Amerithrax investigation that Bruce Ivins acted alone in carrying out the attacks.

Shortly after the McClatchy article was published, I provided this perspective on the new revelations it contained:

> The presence of silicon and how it may have gotten into the anthrax material has been a point of great controversy throughout the entire investigation. This question is important because the chemical nature of the silicon and the level at which it is present is presumed to be an indicator of whether the anthrax spores have been “weaponized” to make them suspend more readily in air so that they are more effective in getting into the small passageways of the lungs of the intended targets of the attack. Early in the investigation, Brian Ross published “leaked” information that the spores had been weaponized through addition of bentonite and that Iraq had a weaponization program that used bentonite. This report turned out to be false, as no evidence for bentonite has been found. A more sophisticated type of weaponizing would rely on mixing the spores with nanoparticles of silica (silica is the common name for the compound silicon dioxide) to make them disperse more easily.
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> The FBI carried out a special form electron microscopy that could identify the location of the silicon in the spores from the attack material. They found that the silicon was in a structure called the the spore coat, which is inside the most outer covering of the spore called the exosporium. If silica nanoparticles had been used to disperse the spores, these would have

> been found on the outside of the exosporuim (see this diary for a discussion of this point and quotes from the scientific literature) because they are too large to penetrate it. No silicon signature was seen on the outside edge of the exosporium. What is significant about the type of silicon treatment suggested in the McClatchy piece is that both high silicon and high tin measurements were found in several samples and that there is an alternative silicon treatment that would involve a tin-catalyzed polymerization of silicon-containing precursor molecules. McClatchy interviewed scientists who work with this process and they confirmed that the ratio of silicon to tin found by the FBI is in the range one would expect if such a polymerization process had been used.
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> What McClatchy doesn’t mention in their report is that it would seem for a polymerization process of this sort, the silicon-containing precursor molecules would be small enough to penetrate the exosporium before being polymerized, or linked together into much larger molecules, once they reached the spore coat. This would mimic the location of silicon incorporated “naturally” into spores.

As the photo above shows, the anthrax spores in the attack material had silicon that was found exclusively in the spore coat and not in the exosporium. This photo is taken from a news article (subscription required) published in March, 2010 in *Science* magazine. I quoted the article in this diary from the same day:

> A more detailed analysis by Joseph Michael and Paul Kotula of Sandia National Laboratories in Albuquerque, New Mexico, contradicted that conclusion. Studying individual spores

> with a transmission electron microscope, they found that the silicon was located within the spore coat, well inside the cell’s exosporium (outermost covering). By contrast, when they looked at surrogate spores weaponized with silica, the silicon was clearly outside the exosporium.
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> But the Sandia study, presented last September to a National Academies panel reviewing the science behind the investigation, still leaves questions. Out of 124 spores from a letter mailed to Senator Patrick Leahy of Vermont, Michael found the silicon-and oxygen signature in 97–78% of the sample. The signature was present in 66% of a sample from a letter to former Senator Tom Daschle and in 65% of spores from a letter sent to the*New York Post*.
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> Out of nearly 200 other anthrax samples from different labs, none came close to displaying such a prominent silicon signature. The highest, in a sample from Dugway Proving Ground in Utah, was 29%. The researchers couldn’t find silicon in the coat of a single spore out of some 300 taken from RMR-1029, the flask in Ivins’s lab identified as the source of the bacteria used in the attacks; they concluded that all the silicon had come from the culture.

Note that the Sandia study found that the attack material had silicon present in the spore coats of a higher percentage of the spores than in any samples they analyzed where silicon had been incorporated into the spore coat during culture. Note also that the only “weaponization” treatment employed in the Sandia study was the treatment of spores with silica nanoparticles which coated the exosporium rather than the spore coat.

As I had suggested after first reading the

McClatchy article, the Hugh-Jones *et. al.* article [full citation: Hugh-Jones ME, Rosenberg BH, Jacobsen S (2011) The 2001 Attack Anthrax: Key Questions, Potential Answers. J Bioterr Biodef S3:001. doi:10.4172/2157-2526.S3-001] describes in detail the chemistry of how the silicon monomers could penetrate the exosporium prior to polymerizing on the surface of the spore coat:

> All the evidence in the public domain is consistent with the concept that the spore coats of the attack anthrax were silicone-coated. Silicone polymers are typically formed by hydrolysis of a silicon compound such as dimethyldichlorosilane (or other silanes with similar substituents), which contains no oxygen. Hydrolysis replaces the chlorine atoms with oxygen to form dimethylsilanol, which polymerizes spontaneously to form polydimethylsiloxane, containing silicon and oxygen in equal amounts. The polydimethylsiloxane chains can then be cross-linked ("cured") to form a three-dimensional silicone coating for encapsulation. This step requires an organotin catalyst such as a dibutyltin dicarboxylate.
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> A procedure of this kind can be envisioned for encapsulating B. anthracis spores. Silane monomers like dimethyldichlorosilane are low-molecular-weight liquids that probably can penetrate the exosporium, the loose-fitting membrane sac that encloses the spore. If silane monomers were added to a suspension of dry spores in an organic solvent, the silane would not contact moisture until it reached the spore coat, where residual moisture diffusing from the core inside the spore would cause hydrolysis, followed by polymerization at the spore coat. The polysiloxane chains that would be formed

> at the spore coat could then be cross-linked to encapsulate the spore. This step would require continued diffusion of moisture from inside the spore, as well as an organotin catalyst. Organotins have low solubility in water but, like silanes, are soluble in organic solvents such as ether, carbon tetrachloride, etc. The ratio of tin to silicon in the attack spores is “about right” for a tin catalyst used to produce a silicone coating, according to a chemist in the field.

As stated previously in the McClatchy article, Hugh-Jones, *et. al.* point out that it would not have been possible to treat anthrax spores with this process at USAMRIID, where Ivins carried out all of his work:

> It would be difficult not to conclude that the spores in the attack letters were prepared for some purpose other than terrorism. Potential procedures that might be applicable for silicone coating of spores, barely touched on here, are complex, highly esoteric processes that could not possibly have been carried out by a single individual. They would require a laboratory with specialized capabilities and expertise not found at USAMRIID, in addition to the possession of the correct strains of B. anthracis Ames associated with flask RMR 1029.

Personnel at USAMRIID all agree that no work with non-aqueous (dry or suspended in organic solvents) anthrax spore preparations is carried out there. The technological ramifications of this are that had Ivins engaged in such work, he would have encountered barriers. His need to decontaminate areas where he worked with dry spore powder would have been greater than areas where he worked with suspensions of spores in water since dry powder would be more likely to disperse over larger portions of the work area. Furthermore, there is no indication that the hot suite where Ivins worked with spores is equipped to handle organic solvents. Safe removal of volatile solvent fumes [ether fumes are responsible for the explosions and fires frequent in amateur meth labs] while still preventing release of spores would require additional air-handling technology that there would have been no reason to have at the USAMRIID hot suites if only water suspensions of spores would be present. Furthermore, the actual polymerization and curing process would be likely to generate organotin vapors that can be quite toxic if not vented properly.

In response to this publication of the details of how anthrax spores could come to have the silicon and tin content observed, even including the observed location of the silicon in the attack material, David Willman attacked this information in Sunday's Los Angeles Times. Here is how Willman describes various recent questions that have been raised about the FBI's data and conclusions:

> One account came from three scientists — long critical of the FBI — whose questions were the subject of a story in the New York Times. Another came from the nonprofit group ProPublica, the PBSdocumentary unit Frontline and McClatchy Newspapers. The coverage highlighted the lingering antagonism toward the FBI among some of Ivins' colleagues at the Army's biowarfare research center at Ft. Detrick, Md.
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> In response to the reports, FBI spokesman Michael Kortan said the bureau stood by its conclusion that Ivins was the perpetrator, "based both on the scientific findings and the results of the extensive traditional criminal investigation."

Note that Hugh-Jones, *et. al.* are described as "long critical of the FBI" and that USAMRIID personnel who disagree with the FBI are painted as having "lingering antagonism toward the FBI". Willman then trots out an FBI spokesman to assure us that the FBI has no doubts about its work or conclusions.

Willman goes to special pains to address the silicon-tin story. After again calling Hugh-Jones, Rosenberg and Jacobsen "longtime critics of the FBI" lest we forget that phrase, Willman goes on to try to impeach Rosenberg by pointing out that she was an early advocate of the theory that Steven Hatfill had been behind the attacks. But Willman's attempt to negate the silicon-tin polymerization theory falls far short of the science:

> Joseph R. Michael, the investigation's top scientist in charge of determining whether the mailed anthrax was treated with additives, acknowledged that it may never be established how tin or another common element, silicon, got into some of the spores. But Michael said that if tin or silicon had been intentionally added, it probably would have coated the exterior surfaces. He said he found trace levels of tin and silicon only inside the spores.

This is the same Joseph Michael of Sandia National Laboratories who produced the image at the top of this post. Recall that in those experiments carried out for the FBI, Michael and his colleagues found that silica nanoparticles added to spores after they were dried resulted in the silicon signature showing up on the exosporium, rather than on the spore coat, as found in the attack material. Michael's work was carried out before the tin-catalyzed silicon polymerization theory was advanced. In his quote to Willman, it's not clear whether Michael has not read the Hugh-Jones *et. al.* paper and its explanation of how the silicon monomers would be expected to penetrate the exosporium before polymerizing at the spore coat or if he is just choosing to claim that such a treatment would be unlikely, so that it would be probable that exogenously added silicon or tin would be found on the exosporium. At any rate, Willman’s quote makes Michael appear entirely unable to consider theories that conflict with his experiment that included only one among the countless number of techniques that could have been employed to introduce the silicon and tin to the attack spores.