MONOATOMIC OXYGEN REVISITED

A NANOSCALE METHOD FOR NON-CONTACT CLEANING OF SENSITIVE MODERN OIL SURFACES USING EFFLUENT OF NEUTRAL OXYGEN ATOMS

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The challenges of modern painted surfaces and the need for non-contact cleaning technologies

The instability of 20th-21st century artworks and unpredictable aging of modern oil paints makes the work of conservation, display, transport and storage a challenge. Soiling and deposition of unwanted materials is particularly damaging to many extremely fragile modern and contemporary painted surfaces due to nontraditional materials and techniques, often leaving porous surfaces without any protective coatings. Painted surfaces are frequently soiled with carbon-based materials: soot, hydrocarbons and organic compounds from pollution, handling, and vandalism, while smoke damage may have irreversible effects within a brief timeframe. Ever increasing exhibition and loan schedules coupled with the current curatorial trend of removing glazing expose extremely vulnerable modern oil paint surfaces to soiling, accidental defacement and vandalism, which may be particularly devastating. It can seriously compromise the integrity and authentic values of the artwork by radically changing the appearance, obfuscating the readability and confusing the meaning of the object itself. If left to dwell, the soiling may act as an initiation point for further material deterioration. In recent years, considerable thought and research has been devoted to primarily to the expansion of new methodologies to clean painted surfaces that require direct physical contact with the artwork and mechanical action of some form with or without a liquid medium (water, organic solvents, silicones, micro-emulsions, gels etc.). However, a cleaning action that requires mechanical contact may be highly problematic on porous, matte, underbound paint or unprimed textile surfaces where soiling cannot be removed safely. Water and other liquid-phase cleaning media may cause irreversible changes due to swelling or the leaching of extractable components and more. Moreover, both “dry” or “wet” cleaning methods risk to transport part of the soiling further into the porous structure of the paint, where the soiling remains permanently trapped, changing the surface morphology and appearance. Many unprotected porous painted surfaces are intolerant of water and other liquid phase cleaning materials or mechanical action and conservators increasingly encounter surfaces ranging from the early 20th century to recent years, where soiling cannot be cleaned at all.

How should these ultra-delicate unprotected painted surfaces be cleaned, if by simply touching them, they could permanently be altered?

Fragile surfaces would greatly benefit from methods that do not require any physical contact and liquid phase medium. At present, laser, plasma, CO_2 snow, and ultrasound methods have limited use treating underbound porous sensitive surfaces. Laser and plasma ablation tools lack selectivity, in some cases require liquid interface medium and lead to excessive heat transfer that pose limitations to their use on sensitive modern materials, confirmed by the discolored appearance of some laser or plasma cleaned surfaces.

Atomic oxygen: disruptive innovation potential through technology transfer from NASA aerospace research

An alternative breakthrough solution may be achieved by developing non-contact cleaning methods that employ neutral monoatomic oxygen, which doesn’t require any physical contact with the surface or any liquid phase cleaning medium to remove carbon-based soiling, soot, hydrocarbons and most unwanted organic materials. Monoatomic oxygen O is one of the three species of oxygen besides diatomic oxygen O_2 and ozone O_3. Atomic oxygen is predominant in the Earth’s thermosphere, where it is produced naturally through the photo-dissociation of molecular oxygen by UV radiation, but is extremely short lived on the ground. In the Low Earth atmosphere (LEO), atomic oxygen is the dominant oxygen species at around 96% and during the past 30 years NASA conducted research on atomic oxygen focused on space and laboratory testing of the spacecraft materials and development of atomic oxygen facilities in simulated space environment vacuum chambers. Several methods can be used to dissociate molecular oxygen into atomic oxygen, such as radio-frequency plasma, photo-dissociation by extreme UV radiation 110-130 nm, laser breakdown, and electric arcing, typically under a partial vacuum. The high degree of reactivity of atomic oxygen makes storing it in tank impossible (where it would react to itself) and requires its production and use to occur simultaneously. In practical terms, it is possible to use atomic oxygen for cleaning treatment either by placing an object in a low-pressure chamber, filled with an atomic oxygen atoms , produced by radio-frequency field, ,laser breakdown, other method, or by using an atmospheric atomic oxygen generator invented in the late 1990’ by Bruce Banks and Sharon Miller at NASA. The vacuum chamber method, currently used in aerospace atomic oxygen research at NASA, ESA and other laboratories has core limitations for conservation application, such as the limited size, limited visual control and access to the objects under the treatment. However, in the proposed process, experimentally proven by B. Banks and S. Miller to remove a lipstick from a defaced Andy Warhol painting “The Bathtub (1961), an atomic oxygen effluent was produced at normal atmospheric pressures, introducing an extraordinary potential application for art conservation. Using this method, the vacuum chamber no longer required and the atomic oxygen source resembles to an air-pen, which can be operated either manually or automated via a sophisticated SNC computerized frame with integrated multi-spectral monitoring and process control.

Forthcoming innovation: non-contact cleaning method using an effluent of neutral oxygen atoms

In target conceptual process, tailored for conservation application, neutral atomic oxygen atoms react in a unique manner with carbon particulate and all carbonaceous soiling compounds (such as soot, grease and diverse hydrocarbons as well as any other organic soiling materials) by converting carbon based and organic soiling into volatile species, mainly CO, CO_2 and H_2O. Atomic oxygen doesn’t react with oxidized inorganic materials, such as pigments and is an instantaneous, and extremely superficial treatment with an activity measurable at the nanoscale due to atomic oxygen’s highly reactive state and extremely brief “life”, that also avoids risk of residual dwelling and propagating in the substrate. In the proposed cleaning mechanism, neutral oxygen atoms exist only for a few milliseconds in normal ambient conditions and removes carbonaceous soiling materials without physical contact with the surface, producing only non-toxic volatile byproducts, and leaves no residues. The concept of the generation mechanism is presented in the diagram (Fig 4). In the proposed concept cleaning process, the monatomic stream is formed by flowing O_2 in an inert noble gas (Ar, He or other) through a high voltage (5-7kV), low current DC arc, which, forms effluent of atomic oxygen atoms at atmospheric pressure through several possible pathways (Fig 3):

A) electron impact dissociation ($e^- + O_2 \rightarrow 2O + e^-$)
B) dissociative attachment ($e^- + O_2 \rightarrow O + O^-$)
C) ionization ($e^- + O_2 \rightarrow O_2+ + 2e^-$ and $e^- + O_2+$ impact $\rightarrow O + O$), which is the dominant process prior to Auger neutralization and impact dissociation to make neutral oxygen atoms

The cathode electrode spot where electrons e^- originate from on the annulus orifice injects electrons e^- into the arc, causing ionization of O_2. However, the O^+_2 ions heading toward the negative electrode are too massive to make the bend and are propelled by the inert carrier gas (He) atoms towards the artwork surface, while the electrons move toward the positive electrode. Inert He gas is used to minimize the gas recombination and to transport the newly created O^+_2 ions to the surface under treatment. The impact dissociation of O^+_2 occurs and two atoms separate. The O^+_2 ions are neutralized by extraction of an Auger electron from the target surface under treatment. The Auger neutralization process (Fig 3) for incoming diatomic oxygen ions is rather complex in that the Auger electron is emitted as a result of a transition in electron states under the influence of the electric field induced by an incoming positive ion. The bulk or surface conductivity can supply electrons back to the treated surface after the Auger electron is extracted or there are sufficient electrons in the effluent that allow the artwork under treatment to maintain a near neutral surface. After the Auger neutralization occurs the neutral diatomic oxygen dissociates upon impact into two neutral atomic oxygen atoms, which is the main active element in the proposed non-contact cleaning method. Upon hitting the surface, the effluent containing neutral atomic oxygen reacts instantly with the first carbon-based materials in its way - carbon/organic soiling - producing volatile by-products such as CO, CO_2 and H_2O vapors, efficiently removing carbon-based soiling, soot, hydrocarbons and most organic unwanted materials through nanoscale ablation. The unreacted O atoms recombine into O_2, or scatter off the surface and the cleaning actions stops when the production of atomic oxygen ceases.

Experimental and treatments

The first application of atmospheric atomic oxygen in art conservation took place in the late 1990s in response to the defacing lipstick smudge on Andy Warhol’s “Bathtub”, where contact/solvent-based cleaning methods could not be used. The defacing mark was left during a cosmetic company party held at the Andy Warhol Museum in 1997. Lipstick samples were given away at the event, and one attendee decided to plant a kiss on the “nude” white-primed surface of the painting. “Of all the paintings there for her to put her lips to, that was the worst one. This painting was so dry that it just sucked everything in” noted Ellen Baxter, the Carnegie Museum of Art’s chief conservator at the time. In response to this “lipstick challenge” B. Banks and S. Miller applied atomic oxygen technology for the first time in an actual conservation treatment. Testing on the mockups was conducted first to remove several lipstick types from white primed canvas. (Fig 6). During the actual treatment, the target red lipstick mark measured 3.3 cm x 3.5 cm. The treatment started with partial solvent pre-cleaning of the lipstick (acetone 1: 3 mineral spirits), taking care not to drive solubilized lipstick into the porous substrate. The remaining lipstick residue, the most complicated component, was successfully removed using the atomic oxygen effluent. Atomic oxygen also removed a thin layer of soiling, exposing a lighter surface, which was subsequently toned by inpainting. Further atomic oxygen experimentation for conservation application was carried out using NASA’s Large Area Atomic Oxygen Exposure Facility, table-top radiofrequency plasma asher, and an experimental atmospheric atomic oxygen source prototype on limited range of artistic media such as modern oils, acrylic paints, watercolors, paper, plaster, limestone, ivory, textile to remove soot, fire damaged carbonized varnish and other carbon based soiling. More tests were carried out to remove inks used in a ballpoint pen and several types of markers.

Conclusions and future work

In conclusion, atmospheric oxygen has an exceptional potential to form the basis for a new non-contact and non-solvent cleaning technology to remove carbon-based soiling, soot, hydrocarbons and most organic unwanted materials from soiled sensitive surfaces. Atomic oxygen could also be an effective emergency response tool for fire and soot damaged artworks. In contrast to water or solvents that propagate and dwell in the substrate, the action of extremely short-lived neutral oxygen atoms is limited to the surface soiling with no penetration into the bulk of a material. Non-contact cleaning produces volatile by-products that are safe to the environment and to the conservator and does not leave residues in the artwork. Materials in high state of oxidation, used in many paints as pigments are typically not affected, and cleaning of organic surfaces is possible and has been proven experimentally, but requires further research . However, as with all tools or techniques it is reasonable to expect that atomic oxygen method may not be suited for all types of surfaces or for every situation. The range of applicability needs tc be studied and will be one of the outcomes of the future research. Further development of atomic oxygen technology for plaster and other unprotected sensitive surfaces requires:

- advancement of the apparatus design and atmospheric oxygen production and spatial dispersion method
- assessment of the effects of atomic oxygen cleaning through the characterization of the physical, chemical and optical properties of painted surfaces treated with atomic oxygen
- In depth understanding of the molecular and nanoscale mechanism and characterization of atomic oxygen cleaning effects on a broad range of paints and substrates.
- The range of applicability needs to be studied and will be one of the outcomes of the future research

Atomic oxygen concept was hatched in aerospace research far ahead of its time and was left suspended at the experimental stage, unavailable to conservators. Further research is required to revisit atomic oxygen potential and transfer it to art conservation as a validated non-contact and non-solvent method with the full benefit of advances in science and technology developed since 1998 when atomic oxygen cleaning concept was first proven at NASA. This is an ongoing research and further advances and developments could fill a critical gap in cleaning methodology for highly problematic porous surfaces, leading to the invention of a ground breaking, noncontact cleaning tool for many sensitive cultural heritage materials, with its greatest potential yet to be realized.

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Fig 1 cleaning action that requires liquid phase medium and mechanical contact may be highly problematic on porous underbound paint surfaces where soiling cannot be removed safely using conventional methods. Detail: underbound porous paint on Edvard Munch “Alma Mater figure study” (1912/14) 122.1×101 cm (left) and (“History” (1911-16) oil on canvas 429x1155 cm (right), Munch Museum, Oslo.

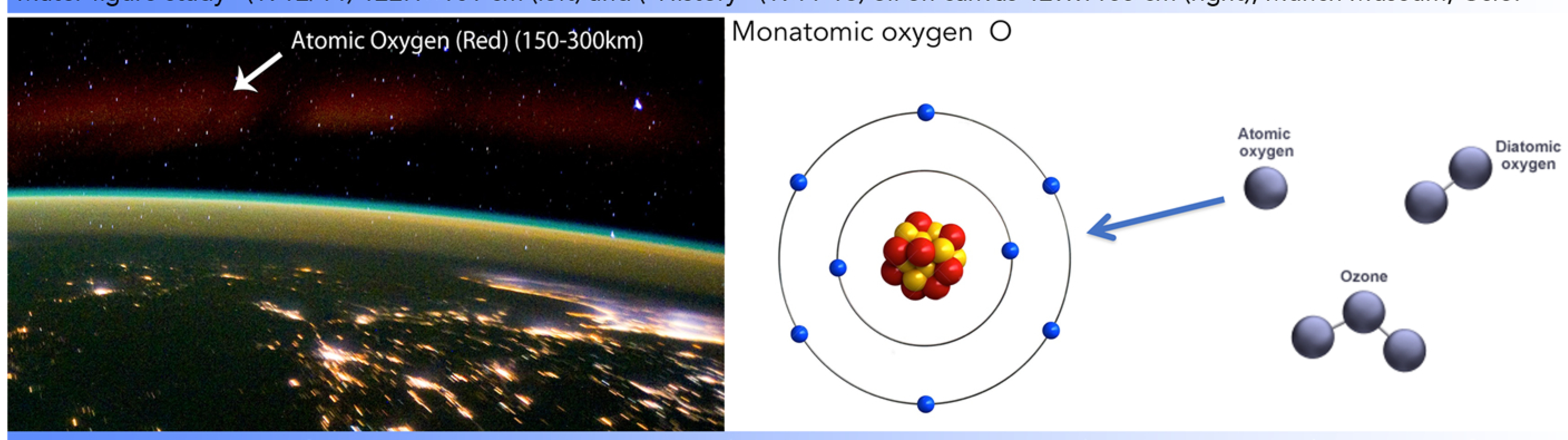

Fig 2 monatomic oxygen formed in Earth’s thermosphere (red glow in the image) interacts readily with many materials on spacecraft flying in low Earth orbit (LEO). All hydrocarbon based polymers and carbon are easily oxidized upon the impact of ~4.5 eV atomic oxygen as the spacecraft ram into the residual atmosphere (left). Oxygen atom: nucleus 8 protons; inner shell 2 electrons, outer shell 6 electrons.

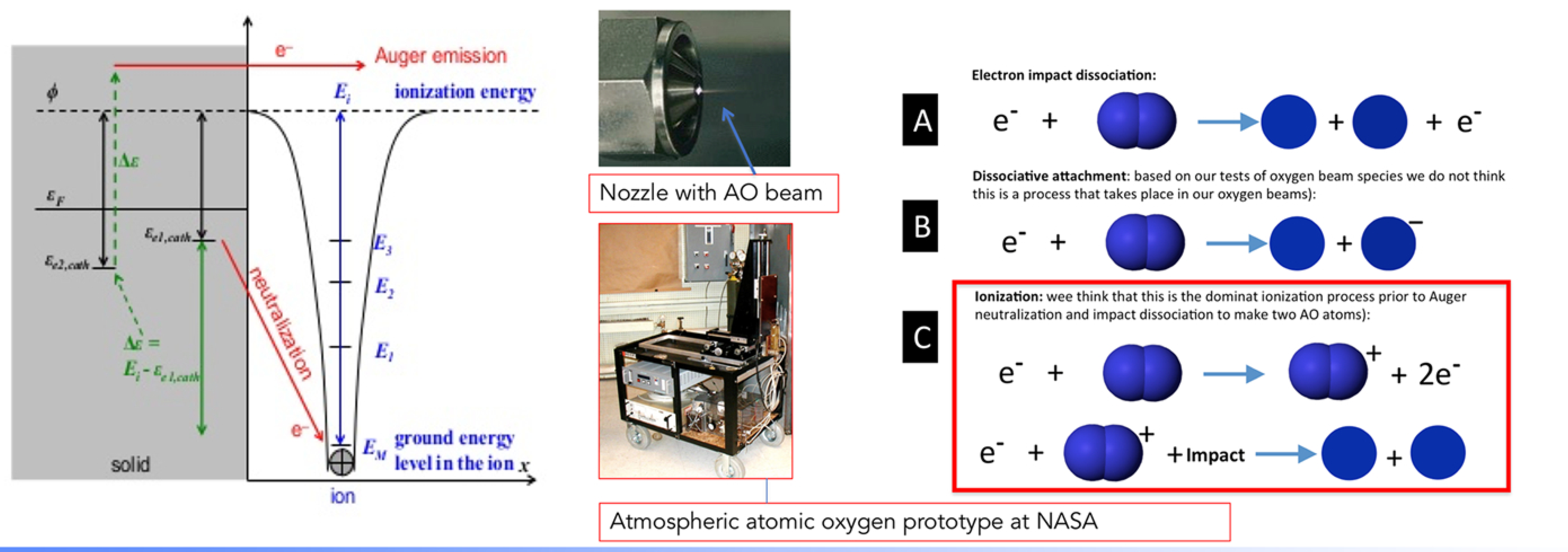

Fig 3 Auger emission process where the electron tunnels from the cathode in the ground state of the ion / neutral, and a second electron receives the excess energy and is emitted (left). Effluent of atomic oxygen atoms at atmospheric pressure is formed through several possible pathways (right). Images: NASA

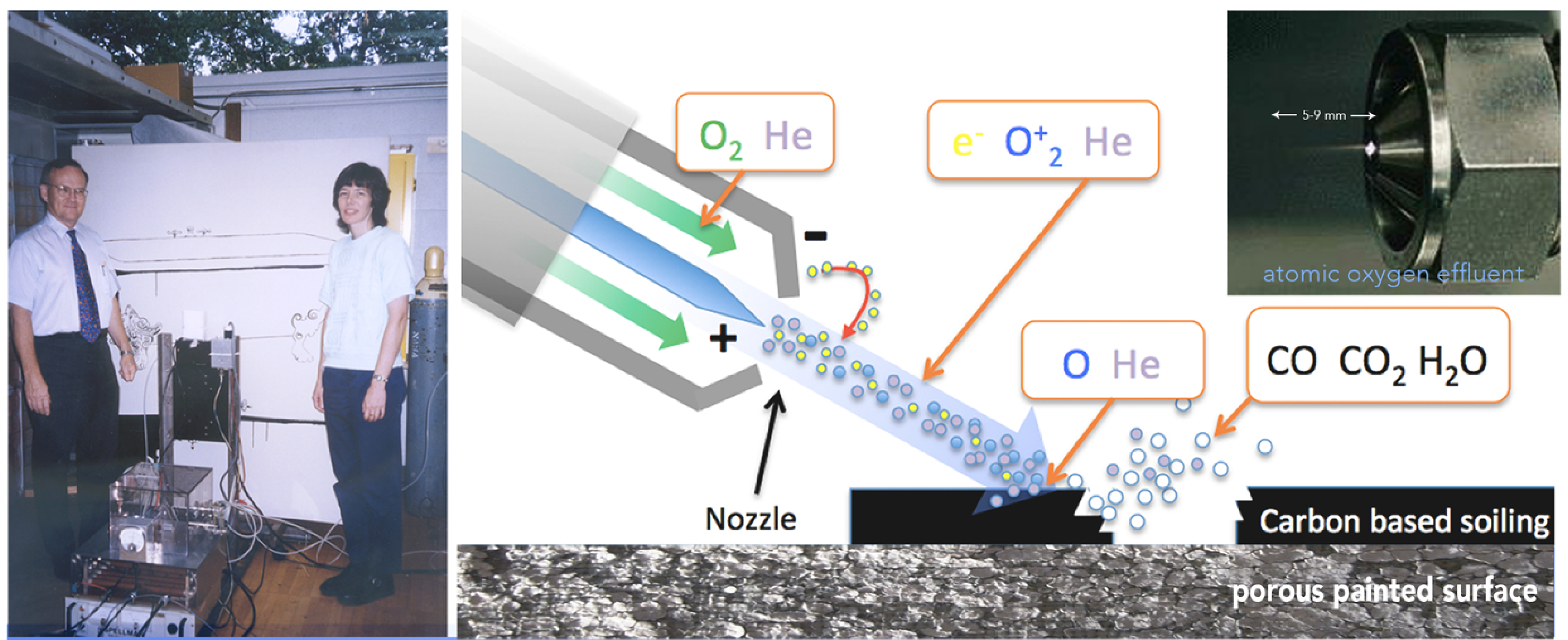

Fig 4 “Bathtub” during treatment using experimental atomic oxygen generator constructed by B. Banks and S. Rutledge at NASA John Glenn Research Center (left) Photo: NASA. Schematic view of atmospheric atomic oxygen generation mechanism (right).

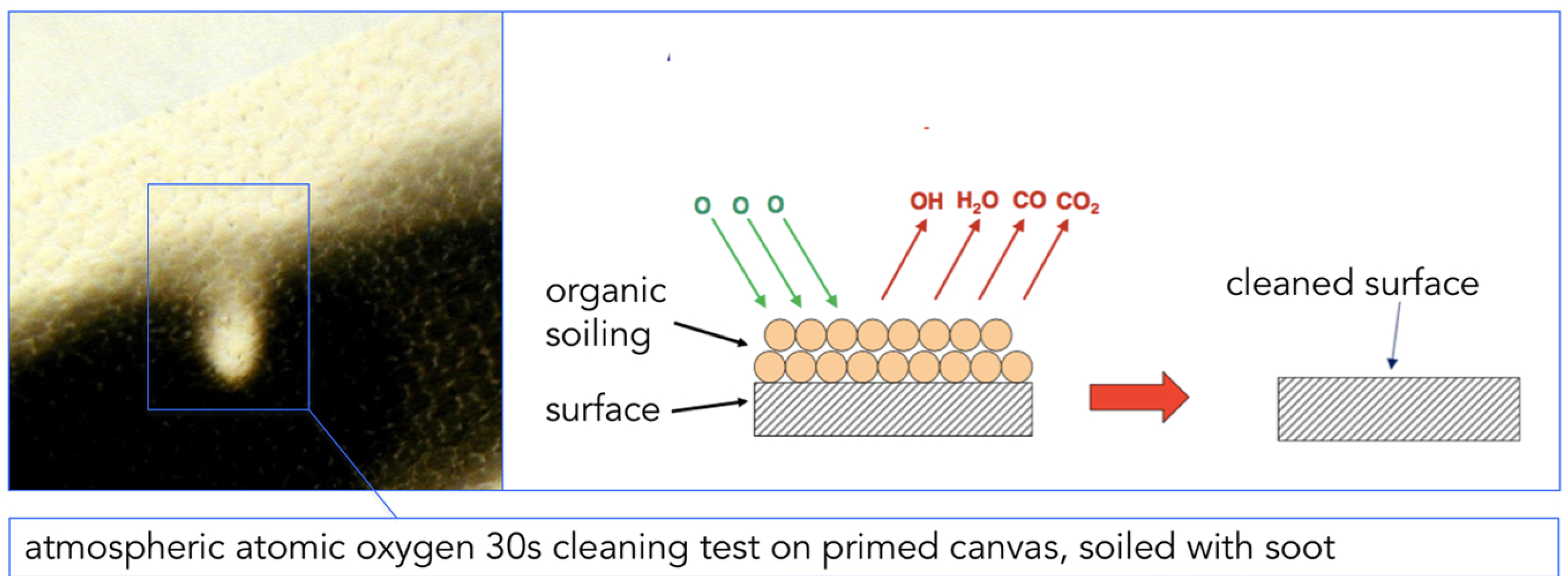

Fig 5 atomic oxygen cleaning test removing soot from canvas porous primed with modern white paint (left). Schematic view of AO interaction with carbon, hydrocarbons and organic compounds in non-contact cleaning process (right). Images: NASA

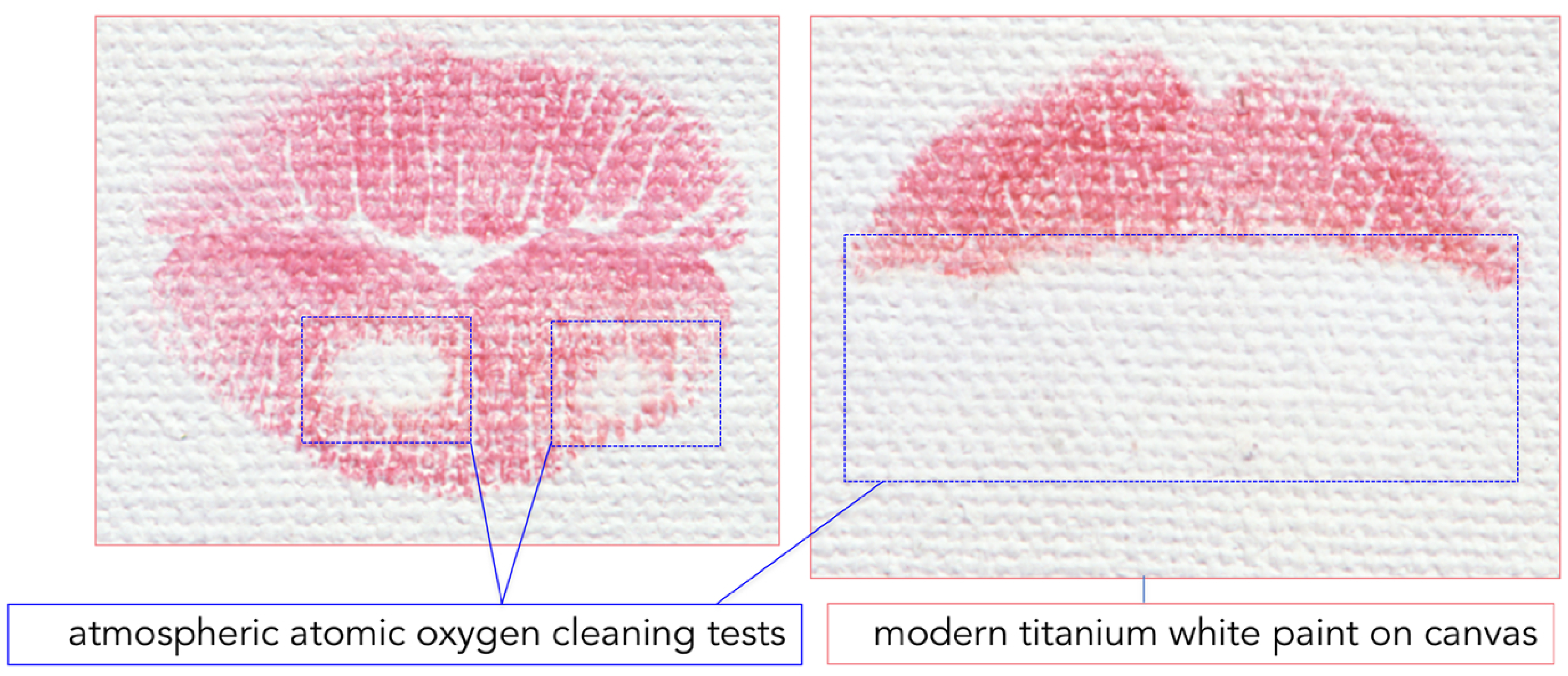

Fig 6 non-contact AO cleaning test on canvas primed with titanium white paint: half of lipstick smudge (left) removed without any changes to the original material. Circular atomic oxygen cleaning tests on the imprint of a lower lip (right). Images: NASA

NASA SAIC From Science to Solutions Technology Arts Sciences TH Köln CMOP Cleaning Modern Oil Paints