

## Review of Cementless Materials for 3D Printing of On- and Off-Earth Habitats

Calabrese, Giuseppe; Hidding, Arwin; Bier, Henriette

DOI [10.1007/978-3-031-50081-7\\_3](https://doi.org/10.1007/978-3-031-50081-7_3)

Publication date 2024

Document Version Final published version

Published in Adaptive On- and Off-Earth Environments

Citation (APA)<br>Calabrese, G., Hidding, A., & Bier, H. (2024). Review of Cementless Materials for 3D Printing of On- and Calabrese, G., Hidding, A., & Bier, H. (2024). Review of Cementless Materials for 3D Printing of On- and Off-Earth Habitats. In A. Cervone, H. Bier, & A. Makaya (Eds.), *Adaptive On- and Off-Earth Environments* (pp. 21-38). (Springer Series in Adaptive Environments). Springer. [https://doi.org/10.1007/978-3-031-50081-](https://doi.org/10.1007/978-3-031-50081-7_3) [7\\_3](https://doi.org/10.1007/978-3-031-50081-7_3)

#### Important note

To cite this publication, please use the final published version (if applicable). Please check the document version above.

#### **Copyright**

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

#### Takedown policy

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.

# *Green Open Access added to TU Delft Institutional Repository*

# *'You share, we take care!' - Taverne project*

*https://www.openaccess.nl/en/you-share-we-take-care*

Otherwise as indicated in the copyright section: the publisher is the copyright holder of this work and the author uses the Dutch legislation to make this work public.

# **Chapter 3 Review of Cementless Materials for 3D Printing of On- and Off-Earth Habitats**



**Giuseppe Calabrese, Arwin Hidding, and Henriette Bier** 

**Abstract** This chapter presents a review of cementless materials for 3D printing, with a specific emphasis on the utilization of volcanic ash in the context of a case study for off-Earth construction. As a highly promising alternative to traditional concrete, selected binders are investigated in relation to volcanic ash for the creation of an alternative concrete. These offer a multitude of compelling advantages, including exceptional sustainability, local availability, and minimal energy use. By opting for volcanic ash-based materials, a significant reduction in resource consumption and pollution can be achieved. The review concludes with a set of considerations aimed at addressing various critical aspects related to volcanic ash-based materials. These considerations encompass vital areas such as binder selection, printability, structural behavior, production optimization, in-situ resource utilization, and sustainability. The goal is to establish a solid foundation for the widespread application of cementless concrete by understanding materials, particularly in the context of utilizing volcanic ash, and thereby fostering a paradigm shift toward more environmentally friendly and resource-efficient construction practices.

## **3.1 Introduction**

The field of 3D printing has made significant progress in the last decade, offering efficient and customizable fabrication of complex structures in various industries such as healthcare and biomedical (Sheoran et al. [2020](#page-21-0)), aerospace and automotive (Salunkhe et al. [2023](#page-20-0)), architecture and construction (Khajavi et al. [2021](#page-20-1); Tay et al. [2017\)](#page-21-1), and everyday consumer products. In construction, 3D printing has the potential to revolutionize traditional building processes by increasing efficiency and providing design flexibility, as well as reducing material waste. However, a critical aspect of

G. Calabrese  $(\boxtimes)$ 

International Research School of Planetary Sciences, Università d'Annunzio, Pescara, Italy e-mail: [giuseppe.calabrese1@unich.it](mailto:giuseppe.calabrese1@unich.it)

G. Calabrese · A. Hidding · H. Bier Delft University of Technology, Delft, Netherlands

<sup>©</sup> The Author(s), under exclusive license to Springer Nature Switzerland AG 2024 A. Cervone et al. (eds.), *Adaptive On- and Off-Earth Environments*, Springer Series in Adaptive Environments, [https://doi.org/10.1007/978-3-031-50081-7\\_3](https://doi.org/10.1007/978-3-031-50081-7_3)



**Fig. 3.1** Rhizome 1.0 prototypes using Vertico's cement-based concrete and robotic system

<span id="page-3-1"></span>

**Fig. 3.2** Rhizome 1.0 material testing using Structural Design and Mechanics, TU Delft expertise, is proving that regolith-based concrete (left) is stronger than regular concrete (right)

<span id="page-3-2"></span>3D printing in construction is the selection and optimization of appropriate materials for extrusion.

For off-Earth applications, the ESA and Vertico co-funded project Rhizome 1.0 implemented 2021–22 has explored 3D printing with cement-based regolith simulant.<sup>1</sup> The project successfully demonstrated the potential of this innovative technique for constructing off-Earth habitats. By utilizing regolith, which is abundantly available on celestial bodies such as the Moon and Mars, Rhizome 1.0 has showcased the feasibility of creating robust and structurally sound structures (Figs. [3.1](#page-3-1) and [3.2\)](#page-3-2) with cement-based regolith concrete, proving to be stronger than regular concrete.<sup>2</sup> The findings of Rhizome 1.0 contribute to the broader understanding of cementbased 3D printing technologies and their applicability for on- and off-Earth habitat construction.

In order to advance this application toward incorporating sustainable cementless materials, the Vertico and ESA-funded project Rhizome 2.0 project that recently

<span id="page-3-3"></span><span id="page-3-0"></span><sup>&</sup>lt;sup>1</sup> Link to Rhizome 1.0 project material studies documentation: [https://docs.google.com/document/](https://docs.google.com/document/d/11wwFsh6__r2Z_zzBL1I80MNLxNW2SjL7kuDADm8vAYg/edit) [d/11wwFsh6\\_\\_r2Z\\_zzBL1I80MNLxNW2SjL7kuDADm8vAYg/edit](https://docs.google.com/document/d/11wwFsh6__r2Z_zzBL1I80MNLxNW2SjL7kuDADm8vAYg/edit).

 $2$  Ibid.

started requires a better understanding of cementless concrete technology. The term 'cement' typically describes materials used for binding aggregates in construction to create solid structures. Portland cement is the most common type, made by heating a blend of limestone, clay, and other components. It's known for its strong binding properties, forming the foundation of concrete. However, alternative binders aim to lessen the environmental impact of traditional Portland cement. The focus on cementless materials involves finding solutions that reduce or eliminate the need for Portland cement, replacing it with alternative binders, which is crucial for advancing sustainable construction practices.

This paper provides a review of the existing literature on cementless materials relevant to Rhizome 2.0, with a specific focus on volcanic ash for 3D printing and highlights the hindrances in the mainstream adoption of the material so far. The literature review for this study encompassed a diverse range of sources focused on the topics of 3D printing for construction, alternative binders, and the sustainability implications of these approaches without the utilization of Portland cement. The review methodology involved a systematic search strategy that targeted relevant databases using specific keywords related to the subject matter. The search was conducted with the aim of identifying papers that discussed the use of alternative binders in the context of 3D printing for habitats, both on Earth and in extraterrestrial environments. The inclusion criteria for the selected papers focused on their relevance to the research question and objectives, as well as the extent to which they provided insights into the material properties, printability, durability, and sustainability aspects of the alternative binders. Papers that explored the application of these binders in construction, particularly in the context of 3D printing, were given priority.

A comprehensive data extraction process was employed to gather relevant information from the selected papers. This included details on the types of alternative binders discussed, their specific properties, their advantages and challenges, and any findings related to 3D printing in habitats. The systematic analysis of the extracted data aimed to identify common themes, trends, and key findings across the selected literature. Quality assessment was considered, taking into account the rigor of the research methods used in the papers, the credibility of the sources, and the relevance of the findings to the research objectives. This step helped ensure that the review included high-quality and reliable information.

The boundaries of the review were defined by the research question and objectives, focusing on the exploration of alternative binders in 3D printing for habitats. While the primary focus was on geopolymer and lime-based materials, other related materials were also considered within the context of sustainability and construction applications. In conclusion, the systematic literature review process involved a structured approach to identify, select, and analyze relevant papers, ensuring a comprehensive exploration of the potential of alternative binders for 3D printing in both off-Earth and on-Earth habitats. The incorporation of a wide range of sources provided a robust foundation for the discussion of the advantages, challenges, and sustainability implications of different binder materials, contributing to the overall goals of the study.

### **3.2 Problem Statement**

The Rhizome 2.0 project aims to achieve a significant advancement in the field of architecture and construction. The objective is to (a) optimize the printing process with cementless concrete i.e., without the use of Portland cement, to ensure the highest quality, precision, and reliability of the printed components, with considerations for dimensional accuracy, surface tectonics, structural integrity, and reduced environmental impact and (b) scaling up the Human–Robot Interaction (HRI) assembly of components approach developed in Rhizome 1.0 (Fig. [3.3](#page-5-0)).

The binder plays a pivotal role in achieving the desired structural behavior and long-term durability of the constructed elements. A comprehensive analysis of various binder options, including the incorporation of volcanic ash materials, is undertaken to identify the most appropriate choice. The aim is to identify a binder material that not only ensures excellent printability but also exhibits robust mechanical performance, including strength, durability, and resistance to external factors such as extreme temperature variations that could be experienced in extreme on-Earth and off-Earth environments.

By undertaking an extensive exploration of the printability of prefabricated components and the selection of an appropriate binder material within the framework of the Rhizome 2.0 project, this research aims to contribute significant insights to the field of construction technology. The outcomes of this study will provide valuable knowledge and practical guidelines for architects, engineers, and researchers, facilitating the adoption of advanced construction methodologies and paving the way for the realization of sustainable, efficient, and structurally sound building systems. The findings will not only impact the domain of off-Earth habitat construction but also hold tremendous potential for revolutionizing construction practices on Earth, ultimately shaping the future of the built environment and processes.

<span id="page-5-0"></span>

**Fig. 3.3** Rhizome 1.0 component mockups and HRI-supported assembly test

The extensive usage of Portland cement in traditional 3D printing materials presents various concerns that require attention. Primarily, the environmental sustainability of Portland cement-based materials is a growing concern due to their high carbon emissions and energy-intensive production methods.<sup>3</sup> Additionally, the widespread use of concrete can be attributed to the accessibility of the raw ingredients for making Portland cement, particularly in developing countries.

In order to surmount these constraints and foster construction practices that are both sustainable and cost-effective, there has been a growing interest in alternative materials. In this context, it is crucial to understand how alternative binders can enhance structural integrity, reduce material dependency, and mitigate environmental impacts in 3D printed structures. By addressing these knowledge gaps, the advancement of sustainable and cost-effective 3D printing methods for on- and off-Earth applications will be implemented.

For instance, Khoshnevis has extensively discussed the potential of 3D printing technology for constructing supportless structures using in-situ materials, using regolith as a potential construction material in extraterrestrial applications. A 3D printing system utilizing microwave power to transform lunar regolith into lava paste and extrude it for structure creation is envisioned. Additionally, the incorporation of polymer powder into the lunar regolith to build green state (uncured) structures is proposed, with post-sintering using microwave power. In this context, it is important to understand fluid dynamics, heat transfer, curing processes, structural properties, and material composition effects under partial-gravity conditions for successful planetary construction using 3D printing. NASA's Human Exploration and Development of Space (HEDS) program, with the goal of building habitats for long-term human occupancy, aligns well with this approach, aiming for in-situ resource utilization and automated construction of habitats in non-terrestrial environments. The paper concludes that 3d printing technology holds significant promise for such construction, making it a viable method for NASA's exploration mission (Khoshnevis [2014\)](#page-20-2).

Robotic concrete fabrication represents a modern construction approach that leverages cutting-edge digital technologies, including 3D printing and computer-aided design, to meticulously craft intricate and accurate concrete structures. Its hallmark lies in the ability to tailor designs and optimize material consumption, making it especially advantageous in various fields, notably architecture. This pioneering method offers unparalleled design flexibility and resource efficiency when compared to conventional construction methods. It carries the potential for remarkable sustainability improvements due to its efficient use of materials, setting it apart from standard construction practices.

However, the current impetus driving the adoption of digital concrete is primarily rooted in cost considerations, which raises the concern of a potential higher carbon footprint. Factors like the increased utilization of paste volume and the overdesign of structures with high clinker cements contribute to a greater environmental impact for

<span id="page-6-0"></span><sup>3</sup> Production of 1 ton of Portland cement is an energy-intensive process that generates about 1 ton of CO2 which represents about 5–7% of the global greenhouse gas produced annually (El-Dieb [2016\)](#page-20-3).

digital concrete compared to traditional concrete solutions. To counterbalance these effects, the paper by Flatt et al. recommends refining material characteristics, such as increasing the size of aggregates, yielding benefits like reduced shrinkage and a more localized use of materials. Exercising careful scrutiny is of utmost importance to ensure that the pursuit of digital concrete doesn't compromise durability, particularly in light of environmental considerations (Flatt [2022](#page-20-4)).

Historically, Portland cement has been the primary binding agent used in construction materials like concretes, mortars, and renders. However, the reliance on Portland cement presents environmental challenges due to its large carbon footprint and energy-intensive manufacturing processes. While Rhizome 1.0 has proven printability with regular Portland cement-based concrete (Figs. [3.1](#page-3-1) and [3.2\)](#page-3-2) the challenge in Rhizome 2.0 is to replace it with cementless materials utilizing an alternative binder to Portland cement. Furthermore, scaling up the HRI-supported assembly approach (Fig. [3.3\)](#page-5-0) needs further consideration.

Volcanic ash, when combined with a Portland cement binder, has emerged as a particularly promising choice in 3D printing applications. Volcanic ash is a material rich in silica and alumina that can be sourced from natural or artificial sources. It exhibits properties that can enhance the performance and structural integrity of 3D printed objects and has shown potential in improving the durability, strength, and workability of construction materials, making it a candidate for replacing Portland cement in 3D printing applications. It can be inferred that the incorporation of supplementary cementitious materials like ground granulated blast furnace slag (GGBS), fly ash, and silica fume results in enhanced rheological, physical, and mechanical characteristics of 3D concrete. This approach not only maintains the energy efficiency and sustainability of the structure but also contributes to its overall improved performance (Samudrala et al. [2023\)](#page-20-5).

Throughout history, the addition of natural or artificial volcanic ash to lime mortars has been successfully practiced. Ancient civilizations utilized volcanic materials, crushed bricks, and pottery fragments mixed with lime as pozzolanic agents (Theodordou et al. [2022](#page-21-2)). The Romans, in particular, extensively used volcanic ash, leading to the development of Roman mortars with exceptional properties. Natural volcanic ash played a crucial role in *opus caementicium*, a precursor to modern concrete (Giavarini et al. [2006\)](#page-20-6). Despite ongoing scientific interest, the complex physical and chemical processes involved in mortar hardening are not yet fully understood. Recent microscopic analysis has provided insights into the composition of ancient Roman mortars, revealing the presence of specific materials and demonstrating the mechanical improvements achieved through the pozzolanic reaction (reaction between volcanic ash and Portland cement) (Seymour et al. [2022](#page-21-3)). This knowledge not only enhances the understanding of ancient Roman mortars but also holds promise for the development of durable and resilient Portland-free sustainable mortars for construction purposes by studying the thermal, rheological, and mechanical properties of volcanic ash-based composites for 3D printing (Low et al. [2021](#page-20-7)).

The potential of volcanic ash extends beyond terrestrial applications, which further highlights the significance of the use of volcanic ash in combination with a binder for

future space exploration and habitation initiatives as a possible cementless material. As described by Schiavone, volcanic ash exists in the form of clays or shales and its chemical composition of volcanic ash consists of a combination of basaltic and trashy-andesitic pyroclastics (Schiavone et al. [2021](#page-21-4)). Volcanic ash can be either utilized in its natural state or produced artificially. It is an inorganic material with a poorly crystalline structure and possesses properties like high thermal stability and a porous form. Natural volcanic ash contains significant amounts of silicon dioxide and aluminum oxide. Its applications range from construction and road building to sanitation and agriculture (Schiavone et al. [2021](#page-21-4)).

A study by Coppola focuses on various aspects related to the production, microstructures, chemical composition, engineering properties, and durability of mixtures that utilize alternative binders instead of Portland cement as well as the application of both traditional and innovative Portland-based mortars with reduced free lime content in the preservation of cultural heritage. The study explores the potential of recycling and waste management as strategies to minimize the consumption of natural resources in construction material production (Coppola et al. [2018\)](#page-19-0).

Other studies have shown that monuments in Rome constructed between the first and fourth centuries AD contain Pozzolane Rosse, which are scoriae erupted by the Alban Hills volcano during the mid-Pleistocene pyroclastic flow. Analysis of mortars from the Trajan Markets in Rome revealed the presence of a crystalline phase called strätlingite, which forms at interfacial regions through the pozzolanic reaction and significantly enhances mechanical properties. Strätlingite's ability to distribute at interfaces positively influences mortar properties, preventing crack propagation and microfractures. These findings not only deepen the understanding of the relationship between structure and properties in ancient Roman mortars but also offer new possibilities for designing innovative, Portland-free, sustainable mortars with enhanced durability and toughness for restoration purposes (Coppola et al. [2018](#page-19-0)).

The study by Dada et al. demonstrates the impact of temperature on the properties of cement mortars incorporating volcanic ash and marble powder, highlighting the potential benefits and limitations of these additives under different temperature conditions (Dada et al. [2021](#page-20-8)).

### **3.3 Volcanic Ash**

Planet Earth as well as Mars and the Moon, exhibit volcanic landforms. On Mars, there are numerous volcanic features, with large shield volcanoes primarily found in the Tharsis Bulge and Elysium Bulge highlands. During explosive volcanic events on Mars, solid rocks and molten slurry were fragmented into fine particles, resulting in the formation of volcanic ash. Similarly, the Moon also showcases volcanic landforms, including volcanic domes, lava plains, and volcanic cones. The lunar maria, which are expansive regions of solidified lava flows, were created by volcanic eruptions that filled impact basins with lava. These volcanic landforms on both Mars and the Moon provide valuable insights into their respective geological histories and past

volcanic activities. The combination of volcanic ash with lime (CaO) and water at room temperature leads to the formation of hydrates that possess hydraulic gelling properties (Malathy [2023](#page-20-9)). As a result, volcanic ash can serve as a suitable ingredient for cement mixing and as an additive for concrete after undergoing the grinding process.

Roman pozzolana cement, which incorporates volcanic ash, exhibits several contrasting characteristics when compared to Portland cement. These include a decreased frost resistance, a lower specific gravity, reduced hydration heat, enhanced corrosion resistance, but higher water demand, and increased shrinkage. Each country's building codes and standards typically allow a maximum replacement of 30–35% when using volcanic ash as a substitute material for costly clinker in blended cement. This limitation is due to the slow pozzolanic reaction of volcanic ash, which slows down the rate of strength development during the early stages. Therefore, there is a requirement to explore alternative binding agents that not only have reduced  $CO<sub>2</sub>$  emissions but also have the capability to effectively utilize large quantities of volcanic ash (Djobo et al. [2017\)](#page-20-10).

#### **3.4 Binders**

In concrete construction, a binder refers to the material that holds the aggregate particles together to form a solid and cohesive mass. Aggregate possesses the largest volume of conventional concrete hence the most effective way to reduce the content of binder is by increasing the volume of aggregate. In the context of using volcanic ash in construction, lime is commonly used as a traditional binder in combination with volcanic ash. The lime reacts with the volcanic ash in the presence of water to form a cementitious compound.

In an extraterrestrial environment like Mars or the Moon other binders in combination with volcanic ash materials include:

1. Magnesium-based Binders: Magnesium oxide (also known as magnesia) can react with carbon dioxide in the presence of water to form magnesium carbonate, which exhibits cementitious properties. Magnesium-based binders have been investigated for use in lunar habitats. A study by Scott (Scott et al. [2020\)](#page-21-5) developed a binder system using magnesium silica that can be created using materials found on the surface of Mars. The researchers combined magnesium oxide, amorphous silica, and water with four different Mars regolith analogs from New Zealand to create mortar cube samples. They also examined how the water-to-cement ratio affected the binder system using a single regolith analog. The findings revealed that the magnesium silica binder-regolith system achieved compressive strengths exceeding 35 MPa at 90 days, making it suitable for various structural applications on Mars. As a side note, polycarboxylate ether superplasticizer is needed to make the material flowable/ workable. This superplasticizer will either have to be produced locally or brought from Earth. For concrete 3D

printing, the workability/pumpability of the material is especially important. In the material preparation phase, magnesium oxide is created from magnesium carbonate.  $CO<sub>2</sub>$  is released in this process, even more than in the production of traditional Portland cement (Shen [2016](#page-21-6)), being thus not a viable alternative.

- 2. Polymer-based Binders: Synthetic polymers or biopolymers can also be explored as potential binders for volcanic ash in extraterrestrial environments (Liu et al. [2022\)](#page-20-11). These binders could possibly be chemically engineered to react with the volcanic ash materials and form a solid matrix. The utilization of biopolymer—a plastic usually made from vegetable starch—and basalt fiber from the Martian surface was utilized in MARSHA created by New York-based architecture firm AI SpaceFactory, in response to NASA's 3D Printed Habitat Challenge. In the printing process, MARSHA demonstrated exceptional precision and cleanliness, presenting a distinctive approach that effectively utilized Martian simulants as resources. The project achieved remarkable autonomy, showcasing the team's ability to operate with minimal external support. Additionally, the biopolymer material exhibited notable compressive and tensile strength, offering promising prospects for future applications on Earth (Roman et al. [2020\)](#page-20-12). The impressive performance of the material opens up possibilities for its utilization in various construction projects and highlights its potential for advancing sustainable building practices. Producing the binder on Mars would require the establishment of manufacturing facilities and resources such as plantations. Furthermore, the system used in Rhizome 1.0 and 2.0 is not printing with polymers and therefore not relevant for this study.
- 3. Geopolymer binders as cement can be made from alumina silicate sources (such as volcanic ash or clay) together with an alkaline reagent and water (Amran et al. [2021\)](#page-19-1). Geopolymer binders present a promising alternative to lime-based binders when volcanic ash materials are used in extraterrestrial environments like Mars or the Moon. Geopolymer binders bring several advantages to the table, including the availability of raw materials, low water requirements, rapid strength development, and exceptional durability and resistance to extreme conditions. Ongoing research and development efforts focus on optimizing geopolymer formulations and comprehending their behavior in unique space environments, paving the way for their application in extraterrestrial construction projects. The material properties of the geopolymer materials are dependent on the source materials. Therefore, the material properties and the durability of the resulting geopolymer will need to be characterized.
- 4. Alkaline-activated-based binders encompass a wider range of materials than the geopolymer binders and are activated by alkaline solutions that show promise since they can be made from regolith. Montes et al. demonstrated that lunar regolith in combination with an alkaline activator could result in a material with a compressive strength ranging from 16.6 to 33.1 MPa (Montes et al. [2015](#page-20-13)). Alkaline activation of Martian or lunar volcanic ash could be investigated, with the resulting materials being characterized in terms of their material properties as well as their durability under extraterrestrial conditions.

5. Carbonate, a substance found in limestone, is abundantly present on both Earth and Mars. Its recent discovery on Mars suggests the existence of water in the planet's past. While the exact quantity of subsurface carbonate on Mars remains uncertain, it signifies the presence of significant water reservoirs beneath the Martian surface. Although Mars currently lacks surface oceans, substantial amounts of water are believed to be concealed beneath its crust, although the exact extent of this water remains poorly understood ([https://www.psi.edu/epo/](https://www.psi.edu/epo/faq/mars.html) [faq/mars.html](https://www.psi.edu/epo/faq/mars.html)).

#### **3.5 Printability**

Printability in the context of volcanic ash materials pertains involves the material's ability to serve as a feedstock for 3D printers, enabling accurate and effective layerby-layer deposition for the creation of desired structures. While volcanic ash materials are commonly used in traditional construction, their applicability in 3D printing is an area of active research. The printability of volcanic ash materials depends on factors such as particle size distribution, flowability, and compatibility with the specific 3D printing technology employed. Ensuring consistent and uniform material flow through the printer nozzle is crucial for achieving precise and reliable prints. The rheological properties, including viscosity and thixotropy, significantly influence the 3D printability of all materials, this sector of research is much needed for volcanic ash materials.

Although there is limited specific literature on the printability of volcanic ash materials in 3D printing, research studies in the field of concrete 3D printing often explore the use of supplementary cementitious materials like fly ash and silica fume and at times in combination with other materials (Putten et al. [2020;](#page-20-14) Bhattacherjee et al. [2021](#page-19-2); Chen et al. [2017](#page-19-3), [2018](#page-19-4), [2021;](#page-19-5) Melichar et al. [2022;](#page-20-15) Peng et al. [2023](#page-20-16); Revelo et al. [2019\)](#page-20-17). These studies investigate the effects of material compositions, mixture designs, and printing parameters on printability and the mechanical properties of 3D printed concrete structures. Investigating the printability of volcanic ash materials is an urgent and essential task. As the construction industry embraces 3D printing technology, understanding how volcanic ash can be effectively used in the additive manufacturing process is crucial.

#### **3.6 Structural Behavior**

The structural behavior of volcanic ash materials pertains to their response when subjected to loads and their overall impact on the structural integrity of a building. Structures incorporating volcanic ash materials demonstrate improved resistance and enhanced long-term performance (Davidovits [2013](#page-20-18)). In Rhizome 2.0 the behavior of these materials under different load scenarios, including static and dynamic loads,

to determine their suitability for specific structural components will be explored. Factors such as material composition, particle size distribution, curing processes, and interfacial bonding characteristics all influence the structural behavior of volcanic ash materials.

To expand on this, further research and experimentation are necessary to investigate the mechanical properties, stress–strain behavior, and long-term durability of volcanic ash materials. This involves conducting comprehensive testing and analysis to evaluate their performance under different environmental conditions and loading conditions. Additionally, the development of computational models and simulation techniques can aid in predicting the structural behavior of volcanic ash materials, providing valuable insights for design optimization and structural analysis.

#### **3.7 Sustainability**

Reducing the reliance on Portland cement offers substantial opportunities for attaining significant sustainability benefits in the construction industry. A promising avenue for achieving this objective is through the application of structural optimization principles, whereby materials are strategically allocated to areas based on their specific requirements, while employing a less dense concentration of materials in other areas. This approach serves a dual purpose: it reduces overall material consumption and contributes to a decrease in printing time, thereby enhancing the efficiency and sustainability of the 3D printing process (Bier et al. [2018\)](#page-19-6).

Structural optimization techniques enable to intelligently allocate materials, ensuring that they are utilized in a targeted and efficient manner. By identifying and concentrating materials in regions where they are most needed, such as loadbearing elements or areas subjected to higher stress levels, an optimized structure can be created (Fig. [3.4](#page-13-0)). Simultaneously, areas that experience lesser stress or have lower material requirements can be manufactured using a less dense approach, resulting in optimized material distribution throughout the printed object.

The benefits of this approach are multifold. Firstly, it leads to a reduction in overall material consumption, as resources are allocated precisely where they are essential, thereby minimizing waste and promoting sustainability. This reduction in material usage aligns with the principles of circular economy and resource efficiency, contributing to a more environmentally responsible construction practice. Secondly, the optimized structural design streamlines the 3D printing process by minimizing unnecessary material deposition and facilitating faster printing speeds. This expedited printing time not only enhances productivity but also reduces energy consumption and associated environmental impacts.

Furthermore, the integration of structural optimization and reduced reliance on Portland cement aligns with the broader goal of sustainable construction practices. Portland cement production is associated with significant carbon dioxide emissions and energy consumption, making its reduction a crucial objective in mitigating the



**Fig. 3.4** Structurally optimized 3D printed structure (top) resulting from structural optimization routines (bottom)

<span id="page-13-0"></span>environmental impact of the construction industry. By exploring alternative materials, such as volcanic ash materials or supplementary cementitious materials like GGBS, fly ash, or silica fume, architects and researchers can advance sustainable 3D printing technologies. These materials offer potential improvements in the rheological, physical, and mechanical properties of 3D printed concrete, while maintaining the energy efficiency and sustainability of the resulting structures.

In conclusion, the integration of structural optimization principles and reduced reliance on Portland cement presents an innovative and sustainable approach to 3D printing in construction. Through targeted material allocation, optimized structures can be achieved, resulting in reduced material consumption and printing time. This approach aligns with the principles of circular economy, resource efficiency, and reduced environmental impact. By exploring alternative materials, architects and researchers can further enhance the sustainability and performance of 3D printed structures, contributing to a more sustainable built environment.

## **3.8 Interdependencies among Machines, Humans, and Materials**

The interrelationships among machines, humans, and materials are pivotal considerations in construction and pioneering projects like Rhizome 1.0 that exemplify the significance of these interconnected elements in shaping the success of innovative construction methodologies (Davidovits [2013\)](#page-20-18). Rhizome 1.0, an ESA-funded initiative, focused on developing an optimized 3D printed structure that encompassed material, structural, and environmental considerations. The collaboration between machines, humans, and materials played a fundamental role in realizing the project's objectives.

By 3D printing Voronoi-based components that are assembled with HRI support a complete human–robot and robot-robot production loop is developed. In this context, the Voronoi-based design describes a parametric approach that allows subdivision of the overall geometry of the habitat into discrete, prefabricated components with material densities based on the structural calculations by generating cells that are smaller at high-stress locations, and larger in low-stress locations (Fig. [3.5](#page-14-0)). The advantage of the Voronoi logic is that the changes in sizes can occur omnidirectional, while approximating the stress concentrations and transitions within the structure. Larger Voronoi cells can be subdivided into smaller cells, creating the potential for hierarchical subdivisions. Beside structural requirements the cells can also be used to integrate other functionalities such as acoustics, hydroponics, electronics, LSS (life support systems) requirements (cables, pipes, ventilation shafts, etc.), and furniture.

The Voronoi cells can be adjusted for the robotic prefabrication process so that the cells meet the production requirements for 3D printing to generate support-free

<span id="page-14-0"></span>

**Fig. 3.5** Voronoi-based material design: computer model (left) and 3D printed prototype (right)

geometries, based on the material properties and the specific production equipment used. The cellular logic can be translated to continuous tool paths allowing for faster and more efficient production of the components by reducing traveling time in the 3d printing process as well as reducing starting and stopping points within the print, ensuring improved printing quality.

Robotic systems, acting as key machines, are instrumental in executing precise and repetitive tasks inherent to the construction process. Equipped with advanced sensors and actuators, these machines automate critical operations, including 3D printing, component assembly, and the utilization of various end-effectors. By integrating these machines into the construction workflow, accuracy, efficiency, and the realization of complex architectural designs are achieved. Human operators and controllers closely collaborate with these machines, translating architectural concepts into tangible structures.

Machines provide precision, automation, and efficiency, while human expertise offers adaptability, creativity, and critical decision-making. Materials serve as the medium through which architectural visions are realized, influencing both the construction process and the final structure's performance. Effective coordination and integration of these interdependent elements enable the development of innovative construction methodologies, pushing the boundaries of architectural possibilities while considering sustainability and environmental impact.

The synergy among machines, humans, and materials in Rhizome 1.0 represents a paradigm shift in the construction industry. The assembly of the prefabricated Voronoi components relies on HRI, which has been developed in collaboration with the Cognitive Robotics (CoR) lab at TU Delft and will be continued in Rhizome 2.0 by scaling up the principles developed so far. For instance, moving and reorienting the  $50 \pm \text{cm}$  high components as a co-manipulation task that couples the human, robot and the environment (Figs. [3.3,](#page-5-0) [3.5,](#page-14-0) and [3.6](#page-16-0)) will be now stacked horizontally and vertically to create larger structures. When the human and the robotic arm are manipulating the component, they form a tightly coupled dynamical system. The design of the componential logic of the Voronoi cells is in part determined by the requirements and limitations of the HRI-supported assembly process.

#### **3.9 Conclusions**

The review of cementless concrete materials revealed that concretes developed using volcanic ash as a precursor demonstrate excellent physical and mechanical properties, surpassing at times those of ordinary Portland cements. They offer a promising alternative for construction materials but much research is lacking. The exploration of various approaches in 3D printing for on- and off-Earth habitats has highlighted the potential for sustainable and innovative construction practices. Each approach brings unique benefits and challenges, and further research and development are necessary to advance these methodologies. The selection of an approach for Rhizome 2.0 takes the



**Fig. 3.6** Stackable 3D printed components

<span id="page-16-0"></span>specific requirements, constraints, and goals of the construction project into consideration, while striving for a balance between material performance, sustainability, and resource utilization.

Despite its availability, low cost, and minimal environmental impact, volcanic ash, a sustainable raw material, has not been fully utilized when compared to other aluminosilicates, and much research is still needed. As a consequence of its very limited exploration, additional investigations are required to address several existing knowledge gaps in the literature, such as temperature dependency, long-term durability monitored under various environmental conditions, etc. Investigations are needed where factors such as the selection of different grades of volcanic ash, optimal volcanic ash content, and printing techniques with the goal of developing a comprehensive understanding of the behavior and performance of volcanic ash composites in various printing scenarios can be achieved.

Future steps will include the evaluation of durability, necessitating comprehensive testing methods including the assessment of carbonation resistance, freeze– thaw resistance, and alkali-silica reaction. The effectiveness of fiber reinforcement, as well as their application as insulating materials, will also be relevant. Furthermore, conducting a comprehensive life cycle assessment (LCA) will provide valuable insights into their sustainability and environmental benefits, supporting the case for adopting this technology in various applications.

Conducting studies on the long-term performance and aging effects will provide insights into their structural integrity, dimensional stability, and resistance to deterioration over extended periods. This knowledge is essential for assessing their reliability and durability in real-world applications. Furthermore, evaluating the fire resistance and thermal properties will help determine their suitability for high-temperature environments, such as fire-resistant structures or thermal insulation applications.

The implementation timeframes in the context of volcanic ash research significantly influence the strategies employed for transferring knowledge and incorporating advancements. In the case of volcanic ash, this will involve gradually introducing the material as a supplementary additive to traditional cement-based mixes, testing its performance, and gradually increasing its proportion. This strategy will allow for a step-by-step adaptation and learning process, ensuring a smooth transition and minimizing potential risks. On the other hand, leapfrogging involves a more rapid and transformative approach by completely replacing Portland cement with volcanic ash-based materials. It is crucial to consider the potential benefits and challenges associated with each approach to ensure a successful and effective transfer of research knowledge in the context of volcanic ash utilization. Rhizome 2.0 will contribute to this research by exploring cementless concrete 3D printing with a particular focus on structural and insulation material properties and componential assembly capabilities at building scale.

In general, the transfer of technology from off- to on-Earth applications involves the integration of knowledge and advancements gained through space exploration and the development of extraterrestrial habitats to enhance technologies and practices on Earth. In the case of volcanic ash, the research conducted for space habitats, exemplified by projects like Rhizome 1.0, holds the potential for driving Rhizome 2.0 sustainable cementless construction methods for both on- and off-Earth applications. The utilization of volcanic ash materials in space environments, characterized by limited resources and stringent environmental constraints, necessitates the development of innovative construction solutions and resource utilization techniques. Through these off-Earth applications, valuable insights are gained that can be adapted and applied to on-Earth projects. By transferring and adapting these technologies and knowledge, pressing environmental concerns can be addressed, reduction of dependence on conventional Portland cement-based materials, and improved efficiency and durability of construction processes.

The field of 3D printing for on- and off-Earth habitats has witnessed diverse approaches and methodologies. One approach explored in the Rhizome 1.0 project involved the use of Portland cement-based regolith simulant as a 3D printing material. This approach demonstrated the feasibility of utilizing local resources for construction, which is crucial for long-duration space missions. The use of Portland cementbased materials offered good structural integrity and durability, providing protection against radiation and thermal stresses. The utilization of volcanic ash materials, as explored in the research discussed above, presents an alternative approach for 3D printing of on and off-Earth habitats. Their utilization aligns with the goal of reducing reliance on Portland cement, which has significant environmental implications due to its high carbon footprint.

When comparing these approaches, it is evident that each offers unique advantages and considerations. The use of cement-based regolith simulant provides a proven and reliable approach that aligns with existing construction practices. Biopolymer basalt composites offer sustainability benefits and superior material strength, which can be advantageous for both extraterrestrial and Earth-based applications, they will be not considered in Rhizome 2.0 because of the employed 3D printing system. Volcanic

ash materials present an opportunity to improve the performance and sustainability of 3D printed structures, offering potential advancements in both material properties and environmental impact.

However, challenges and further research are required for each approach. For cement-based regolith simulants, the availability and production of suitable binders in extraterrestrial environments need to be addressed. Volcanic ash materials necessitate detailed characterization and optimization to achieve desired printability and structural behavior.

Magnesium-based binders require superplasticizers to create workable concrete. Finding a suitable superplasticizer that can locally be produced would be an option, but this needs to be further investigated. Also, a large amount of C02 is released in the production of manganese oxide from manganese carbonate, which is outside of the proposed research. Biopolymer binders would require plant cultivations, or transporting the binder from Earth. Also, the extrusion process requires a different extrusion system than the one available for the Rhizome 2.0 project. Biopolymer materials may require further investigation into their long-term durability and suitability for different environmental conditions. Geopolymer binder technology involves the use of inorganic polymers as a binder in construction materials instead of traditional cement-based binders. Geopolymers offer several advantages, including higher durability, fire resistance, and lower carbon emissions compared to cement as well as reduced energy usage when compared to Portland cement.

The comprehensive exploration of alternative binders in this study has shed light on the potential application of lime as a viable material for Rhizome 2.0. Notably, the availability of carbonate, including limestone, on Mars has been reported by reputable sources such as the Planetary Science Institute of Tucson, Arizona. This intriguing finding opens up new avenues for considering a lime-based approach, akin to its terrestrial counterparts, in the construction of habitats and infrastructure on Mars.

Lime possesses several advantageous properties that make it an attractive candidate for Rhizome 2.0. Its hydraulic nature allows for the formation of durable and robust structures, while lime-based materials have a long history of successful application in terrestrial construction, offering a wealth of knowledge and established construction techniques that could be adapted and optimized for extraterrestrial contexts. However, the suitability and performance of lime-based materials in Martian conditions cannot be assumed without rigorous investigation and experimentation. Factors such as the specific mineralogical composition of Martian carbonate deposits, the presence of impurities, and potential variations in the process of lime production in extraterrestrial settings need to be thoroughly evaluated. These investigations should encompass detailed material characterization, compatibility studies, and performance assessments to ensure the desired mechanical strength, durability, and compatibility with other construction elements. Moreover, the specific challenges posed by the Martian environment, including extreme temperature fluctuations, low atmospheric pressure, and radiation exposure, must be considered in the design and optimization of lime-based construction materials for Rhizome 2.0. Tailoring the material composition, formulation, and curing methods to address these

challenges is paramount to achieving the desired structural integrity and longevity of the constructed habitats.

In conclusion, the presence of carbonate resources on Mars and the favorable properties of lime make a compelling case for considering a lime-based approach as a potential solution for Rhizome 2.0. However, it is important to note that limebased cements require significant energy inputs, necessitating local energy generation mechanisms. Moreover, additional research, experimentation, and technological development are crucial to validate the feasibility and optimize the performance of lime-based materials within the unique and challenging Martian environment.

Alternatively, geopolymers offer promising material properties with reduced energy requirements compared to the lime-based approach. Therefore, conducting prototyping experiments with both materials would yield valuable data pertaining to printability, material properties, durability, and other relevant factors. It is essential to emphasize that the specific material properties of both lime-based and geopolymer mixes will be highly dependent on the characteristics of the regolith simulant employed. By undertaking such endeavors, a considerable contribution to the advancement of sustainable and robust construction practices for future extra-/ terrestrial habitats is achieved.[4](#page-19-7) 

**Acknowledgements** This paper has profited from the contribution of students, researchers, and practitioners involved in the Rhizome 1.0 and 2.0 projects co-funded by ESA and Vertico as part of the co-funded research scheme of the ESA's Discovery program, under contract ESA AO/2-1749/ 20/NL/GLC.

#### **References**

- <span id="page-19-1"></span>Amran et al (2021) Long-term durability properties of geopolymer concrete: an in-depth review. Case Stud Constr Mater 15. <https://doi.org/10.1016/j.cscm.2021.e00661>
- <span id="page-19-2"></span>Bhattacherjee et al (2021) Sustainable materials for 3D concrete printing. Cement Concr Compos 122. <https://doi.org/10.1016/j.cemconcomp.2021.104156>
- <span id="page-19-6"></span>Bier H, Liu Cheng A, Mostafavi S, Anton A, Bodea S (2018) Robotic building as integration of design-to-robotic-production and-operation. Robot Building 97–120
- <span id="page-19-3"></span>Chen Y et al  $(2017)$  A critical review of 3D concrete printing as a low  $CO<sub>2</sub>$  concrete approach. Heron 62:167–194. <https://api.semanticscholar.org/CorpusID:145922661>
- <span id="page-19-4"></span>Chen Y et al (2018) Feasibility of using low  $CO<sub>2</sub>$  concrete alternatives in extrusion-based 3D concrete printing. First RILEM international conference on concrete and digital fabrication digital concrete 2018. [https://doi.org/10.1007/978-3-319-99519-9\\_25](https://doi.org/10.1007/978-3-319-99519-9_25)
- <span id="page-19-5"></span>Chen Y et al (2021) 3D printing of calcined clay-limestone-based cementitious materials. Cement Concr Res 149. <https://doi.org/10.1016/j.cemconres.2021.106553>
- <span id="page-19-0"></span>Coppola L et al (2018) Binders alternative to Portland cement and waste management for sustainable construction-part 1. J Appl Biomater Funct Mater. 16(3):186–202. [https://doi.org/10.1177/228](https://doi.org/10.1177/2280800018782845) [0800018782845.](https://doi.org/10.1177/2280800018782845) PMID: 29996741

<span id="page-19-7"></span><sup>4</sup> Link to Rhizome 1.0 and 2.0: <http://cs.roboticbuilding.eu/index.php/Shared:RhizomeReview6> and <http://cs.roboticbuilding.eu/index.php/Rhizome2>.

- <span id="page-20-8"></span>Dada H et al (2021) Influence of temperature on the rheological behaviour of eco-mortar with binary and ternary cementitious blends of natural pozzolana and marble powder. Powder Technol 384:223–235. <https://doi.org/10.1016/j.powtec.2021.02.019>
- <span id="page-20-18"></span>Davidovits J (2013) Geopolymer Cement a review. Geopolymer Sci Techn, Technical Paper #21, 2013, Geopolymer Institute Library. [www.geopolymer.org](http://www.geopolymer.org)
- <span id="page-20-10"></span>Djobo et al (2017) Volcanic ash-based geopolymer cements/concretes: the current state of the art and perspectives. Environ Sci Pollut Res 24:4433–4446. [https://doi.org/10.1007/s11356-016-](https://doi.org/10.1007/s11356-016-8230-8) [8230-8](https://doi.org/10.1007/s11356-016-8230-8)
- <span id="page-20-3"></span>El-Dieb A (2016) Cementless concrete for sustainable construction. MOJ Civil Eng 1(2):32. [https://](https://doi.org/10.15406/mojce.2016.01.00008) [doi.org/10.15406/mojce.2016.01.00008](https://doi.org/10.15406/mojce.2016.01.00008)
- <span id="page-20-4"></span>Flatt J et al (2022) On sustainability and digital fabrication with concrete. Cement Concr Res 158. <https://doi.org/10.1016/j.cemconres.2022.106837>
- <span id="page-20-6"></span>Giavarini et al (2006) Mechanical behaviour and properties. In: Kourkoulis SK (eds) Fracture and failure of natural building stones. Springer, Dordrecht. [https://doi.org/10.1007/978-1-4020-507](https://doi.org/10.1007/978-1-4020-5077-0_7) [7-0\\_7](https://doi.org/10.1007/978-1-4020-5077-0_7)
- <span id="page-20-1"></span>Khajavi et al (2021) Additive manufacturing in the construction industry: the comparative competitiveness of 3D concrete printing. Appl Sci 11(9):3865. [https://doi.org/10.3390/app110](https://doi.org/10.3390/app11093865) [93865](https://doi.org/10.3390/app11093865)
- <span id="page-20-2"></span>Khoshnevis B (2014) Automated construction by contour crafting—related robotics and information technologies. Autom Constr 13(1):5–19. <https://doi.org/10.1016/j.autcon.2003.08.012>
- <span id="page-20-7"></span>Low et al (2021) Composite materials: manufacturing, properties and applications:29. [https://doi.](https://doi.org/10.1016/C2019-0-00666-8) [org/10.1016/C2019-0-00666-8](https://doi.org/10.1016/C2019-0-00666-8)
- <span id="page-20-11"></span>Liu J et al (2022) In-situ resources for infrastructure construction on Mars: a review. Int J Transportation Science and Technology, Volume 11, Issue 1, 2022. Pages 1–16. ISSN 2046–0430. [https://doi.org/10.1016/j.ijtst.2021.02.001.](https://doi.org/10.1016/j.ijtst.2021.02.001)
- <span id="page-20-9"></span>Malathy et al (2023) Lime based concrete and mortar enhanced with pozzolanic materials–State of art. Constr Build Mater 390. <https://doi.org/10.1016/j.conbuildmat.2023.131415>
- <span id="page-20-15"></span>Melichar J et al (2022) Study of the interaction of cement-based materials for 3D printing with fly ash and superabsorbent polymers. Buildings 12. <https://doi.org/10.3390/buildings12112008>.
- <span id="page-20-13"></span>Montes et al (2015) Evaluation of lunar regolith geopolymer binder as a radioactive shielding material for space exploration applications. Adv Space Res. [https://doi.org/10.1016/j.asr.2015.](https://doi.org/10.1016/j.asr.2015.05.044) [05.044](https://doi.org/10.1016/j.asr.2015.05.044)
- <span id="page-20-16"></span>Peng Y et al (2023) Development of alternative cementitious binders for 3D printing applications: a critical review of progress, advantages and challenges. Compos B Eng 252:110492. [https://](https://doi.org/10.1016/j.compositesb.2022.110492) [doi.org/10.1016/j.compositesb.2022.110492](https://doi.org/10.1016/j.compositesb.2022.110492)
- Planetary Science Institute. Mars—Frequently Asked Questions. [https://www.psi.edu/epo/faq/](https://www.psi.edu/epo/faq/mars.html) [mars.html.](https://www.psi.edu/epo/faq/mars.html) Accessed 17 July 2023
- <span id="page-20-14"></span>Putten D et al (2020) 3D printing of cementitious materials with superabsorbent polymers: a durable solution? In: 4th International RILEM conference on microstructure related durability of cementitious composites (Microdurability). [http://resolver.tudelft.nl/uuid:9d7c9a54-6f01-42ff-a510-](http://resolver.tudelft.nl/uuid:9d7c9a54-6f01-42ff-a510-1f57dbed537a) [1f57dbed537a](http://resolver.tudelft.nl/uuid:9d7c9a54-6f01-42ff-a510-1f57dbed537a)
- <span id="page-20-17"></span>Revelo et al (2019) 3D printing of kaolinite clay with small additions of lime, fly ash and talc ceramic powders. Process Appl Ceram. <https://api.semanticscholar.org/CorpusID:210522500>
- <span id="page-20-12"></span>Roman M et al (2020) 3D-printing lunar and martian habitats and the potential applications for additive construction. In: International conference on environmental systems. [https://hdl.han](https://hdl.handle.net/2346/86486) [dle.net/2346/86486](https://hdl.handle.net/2346/86486)
- <span id="page-20-0"></span>Salunkhe et al (2023) Current trends of metal additive manufacturing in the defense, automobile, and aerospace industries. In: Advances in metal additive manufacturing. Woodhead Publishing, pp 147–160. <https://doi.org/10.1016/B978-0-323-91230-3.00004-4>
- <span id="page-20-5"></span>Samudrala et al (2023) 3D-printable concrete for energy-efficient buildings. Energies 16:4234. <https://doi.org/10.3390/en16104234>
- <span id="page-21-4"></span>Schiavone N et al (2021) Pozzolan based 3D printing composites: from the formulation till the final application in the precision irrigation field. Materials 14:43. [https://doi.org/10.3390/ma1](https://doi.org/10.3390/ma14010043) [4010043](https://doi.org/10.3390/ma14010043)
- <span id="page-21-5"></span>Scott A et al (2020) Magnesium\_based cements for Martian construction. J Space Eng 33(4):04020019. <https://doi.org/10.1061/%28ASCE%29AS.1943-5525.0001132>
- <span id="page-21-3"></span>Seymour et al (2022) Reactive ceramic aggregates in mortars from ancient water infrastructure serving Rome and Pompeii. Cell Rep Phys Sci 3(9):101024, ISSN 2666-3864. [https://doi.org/](https://doi.org/10.1016/j.xcrp.2022.101024) [10.1016/j.xcrp.2022.101024](https://doi.org/10.1016/j.xcrp.2022.101024)
- <span id="page-21-6"></span>Shen W et al (2016) Is magnesia cement low carbon? Life cycle carbon footprint comparing with Portland cement. J Clean Prod 131. <https://doi.org/10.1016/j.jclepro.2016.05.082>
- <span id="page-21-0"></span>Sheoran et al (2020) Bio-medical applications of additive manufacturing: a review. Procedia Manuf 51:663–670. <https://doi.org/10.1016/j.promfg.2020.10.093>
- <span id="page-21-1"></span>Tay et al (2017) 3D printing trends in building and construction industry: a review. Virtual Phys Prototyp 12(3):261–276. <https://doi.org/10.1080/17452759.2017.1326724>
- <span id="page-21-2"></span>Theodordou et al (2022) New evidence of early use of artificial pozzolanic material in mortars. J Archaeol Sci 40(8):3263–3269. <https://doi.org/10.1016/j.jas.2013.03.027>