1 Crystalline silica content of natural, engineered, and synthetic stone products and their 2 relation to silicosis policy development 3  $Dominique\ Tanner^{1\#},\ Lloyd\ Thomas\ White^{1^*+},\ David\ Dennis\ Tettey\ Noi^2,\ Vinod\ Gopaldasani^2$ 4 5 6 <sup>1</sup>Environmental Futures, School of Science, University of Wollongong, Wollongong, NSW, 7 Australia. 8 <sup>2</sup>Center for Occupational Public and Environmental Research in Safety and Health 9 (COPERSH), School of Health and Society, University of Wollongong, Wollongong, NSW, 10 Australia. 11 #Current Affiliation: Geoscience Australia, Canberra, ACT, Australia <sup>+</sup> Current Affiliation: Rock Records Pty. Ltd., and Research School of Earth Sciences, 12 13 Australian National University, Canberra, ACT, Australia \*Corresponding author: <a href="mailto:dr.ltwhite@gmail.com">dr.ltwhite@gmail.com</a> 14 15 16 Statement: This paper is a preprint submitted to EarthArXiv. It is currently undergoing peer 17 review in "Next Research". 18

19 Crystalline silica content of natural, engineered, and synthetic stone products and their 20 relation to silicosis policy development 21  $Dominique\ Tanner^{1\#},\ Lloyd\ Thomas\ White^{1^*+},\ David\ Dennis\ Tettey\ Noi^2,\ Vinod\ Gopaldasani^2$ 22 23 24 <sup>1</sup>Environmental Futures, School of Science, University of Wollongong, Wollongong, NSW, 25 Australia. <sup>2</sup>Center for Occupational Public and Environmental Research in Safety and Health 26 27 (COPERSH), School of Health and Society, University of Wollongong, Wollongong, NSW, 28 Australia. 29 #Current Affiliation: Geoscience Australia, Canberra, ACT, Australia 30 <sup>+</sup> Current Affiliation: Rock Records Pty. Ltd., and Research School of Earth Sciences, 31 Australian National University, Canberra, ACT, Australia 32 \*Corresponding author: dr.ltwhite@gmail.com 33 34 **ABSTRACT** 35 Crystalline silica minerals – quartz, cristobalite, and tridymite – are hazardous when inhaled. 36 They are at least an order of magnitude more toxic than crystalline silica-free inert mineral 37 dusts. Workplace exposure to hazardous levels of crystalline silica is entirely preventable, yet 38 accelerated silicosis is emerging in developed countries, from the fabrication of crystalline 39 silica-rich natural and synthetic stone materials (including engineered stone). The Australian 40 government responded to this crisis through legislation to first limit, and then later ban crystalline silica in engineered stone, while other governments have focused their efforts on 41

workplace monitoring and enforcing safety regulations. To approach this issue sensibly,

policymakers must know the range of crystalline silica in natural rocks, engineered stone and other synthetic stone products such as porcelain – since these materials typically contain >1 vol.% crystalline silica and are commonly fabricated by stonemasons. Workers in other industries, such as mining, tunnelling, and construction are also routinely exposed to dust containing crystalline silica from natural rocks and concrete. Here, we review and compare the crystalline silica contents of natural rocks and synthetic stone products to demonstrate the efficacy of limits on the amount of crystalline silica in products ("thresholds") relative to other dust control measures. We review molecular-scale determinants of silica toxicity and suggest that the fabrication of alternative, and newer generations of engineered stone products may also pose a significant health risk.

**KEYWORDS:** silicosis, dust, fabrication, lung disease, rock, dimension stone

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1. INTRODUCTION

Crystalline silica (Table 1) is abundant and widespread throughout the natural world, but toxic to humans if fine particles are inhaled. Comprising ~12 volume percent (vol. %) of the continental crust, quartz is the second most abundant mineral on Earth's surface after feldspars (Ronov and Yaroshevsky, 2016). Given its prevalence in nature and its durability, crystalline silica is a common constituent of natural dimension stones. Crystalline silica is also added to synthetic products to simulate the properties of natural dimension stone, including concrete, bricks, terrazzo, porcelain, and engineered stone slabs (Table 1). Most human exposure to respirable crystalline silica (RCS) occurs in the workplace (Southard et al., 2014), including the fabrication and finishing of natural rock and synthetic stone slabs. With appropriate occupational safety measures in place, silicosis is a preventable occupational disease (Southard et al., 2014). In the public health literature, crystalline silica typically refers to quartz, cristobalite, tridymite, and sometimes 'tripoli' (IARC 1997; 2012; Leung et al., 2012; Southard et al., 2014) as these are used in industrial applications (Table 1). Crystalline silica is not toxic to humans when grains are bound within a solid rock – but it can be when it is fabricated (e.g., cut, ground, polished) and inhaled as RCS (Leung et al., 2012; Turci et al., 2016; Leinardi et al., 2020; Pavan et al., 2020; Bellomo et al., 2023). The definition of what is 'respirable' is variable within the literature. The international convention on air quality particle size fraction for health-related sampling defines the respirable fraction for healthy adults as a cumulative log normal distribution with a median

diameter of 4.25 µm and a geometric standard deviation of 1.5 (ISO 7708, 1995). Many people refer to particles with a mass median aerodynamic diameter of <3-4 μm as being the respirable fraction (IARC 1997; Maciejewska 2008; Brown et al., 2013), while others report the particle size is <10 μm (Leung et al., 2012). This discrepancy perhaps reflects differences in reporting the average or median respirable particle size (e.g., <~4 μm), compared to reporting an approximation of the range of all respirable particles (e.g., <10 μm). The discrepancy could also arise because the size of particles controls their depositional efficiency in different parts of the respiratory system, which differs between oral and nasal breathing (e.g., Figure 4 in Plumlee et al., 2006), as well as between adults and children (e.g., Brown et al., 2013). Finer particles are deposited more efficiently in the deeper parts of human lungs, where they cannot be removed by mucociliary clearance (i.e., swallowing) (ICRP 1994; Plumlee et al., 2006). Particles deposited in the distal airways can only be removed by alveolar macrophages (immune cells in the distal lung) (Joshi et al., 2018) through phagocytosis (a process where cells ingest foreign particles to remove them) (Uribe-Querol and Rosales 2022). Phagocytosis of RCS particles in the lung results in inflammation and fibrosis mediated by inflammatory cytokines (Leung et al., 2012). As crystalline silica is not effectively cleared through phagocytosis, it continues to accumulate and translocate (Southard et al., 2014) and is a source of ongoing inflammation and fibrosis (Leung et al., 2012). With workplace exposure to hazardous levels of RCS, this process can progress to lung diseases, including silicosis and lung cancer (Lueng et al., 2012; Southard et al., 2014).

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High incidences of silicosis typically occur in countries that have limited regulation and surveillance around long-term occupational exposure to silica dust (Hoy et al., 2022). This commonly reflects workplace exposure in areas such as mining, stonecutting, and benchtop fabrication, as well as the manufacture of dental prostheses, and stonewashed jeans (Hoy et al., 2022). Although the World Health Organisation and International Labour Organisation launched a joint campaign in 1995 to eliminate silicosis by 2030 (The Lancet Respiratory Medicine, 2019), occupational exposure to respirable crystalline silica dust—and consequently, the incidence of silicosis—remains widespread globally. For example, the prevalence of silicosis among South African gold miners has not significantly improved since 1984 (Knight et al., 2015; 2020). While silicosis is a global problem, presently the *reported* burden of disease is greatest in countries with a middle to high sociodemographic index (Hoy et al., 2022; Liu et al., 2023).

Over the last decade, developed countries have seen an increase in cases of accelerated silicosis, where silicosis develops after a relatively short exposure period (Hoy et al., 2022; Liu et al., 2023). The prevalence of accelerated silicosis in developed countries has in many cases, been attributed to the fabrication and customisation of crystalline silica-rich engineered stone countertops (Pavan et al., 2016). A recent Australian study of the stone benchtop industry identified silicosis in 22% of workers; while the average exposure period was 12 years, for one person, their exposure was as little as three years (Table 2)(Hoy et al., 2023). Table 2 demonstrates that this prevalence of silicosis is broadly comparable to that of workers in a crystalline silica-rich underground gold mine in Jiangxi, China (Tse et al., 2007).

Please Insert Table 2.

To mitigate the risk of accelerated silicosis for workers, public health regulators can:

- Reduce workplace exposure limits for RCS and mineral dust. For example, exposure limits for RCS ranged between 0.025 to 10 mg/m³ from different national regulators from 37 countries over the past thirty years (Maciejewska 2008; Rey-Brandariz et al., 2023). Most developed countries now regulate RCS at limits between 0.025-0.1 mg/m³ where the most commonly set limit set by different authorities is 0.05 mg/m³ (Rey-Brandariz et al., 2023).
- Ban the sale of stone products containing a threshold value of crystalline silica. For example, Australia is the first country to ban the use, supply, and manufacture of engineered stone products "containing > 1 w/w% crystalline silica" (Safe Work Australia 2024a).
  - Introduce controls and modify practices (e.g., wet cutting, ventilation systems, respiratory protective devices, training) for workers fabricating products that contain a defined maximum amount of crystalline silica. For example, Australia has introduced legislation to control the processing of "crystalline silica substances" (material that contains at least 1% crystalline silica, determined as a weight/weight concentration) (Safe Work Australia 2024b). Previous legislation in the Australian state of Victoria used a maximum value of 40 w/w% crystalline silica (Chief Parliamentary Counsel 2021), as it was proposed that natural "benchtop materials such as marble, granite, and concrete contain 2-40% crystalline silica" (Safe Work Australia 2023).
- Increase compliance with legislation through monitoring and licensing.

Presently, there is no readily available literature summarising the range of crystalline silica in common natural dimension stone products or comparing the range of crystalline silica between natural rock and synthetic stone products. We aim to address this knowledge gap. Our review of the crystalline silica content of natural dimension stone and synthetic stone products (Supplementary File 1) will help regulators, companies, and workers understand which products are likely to contain more than 1 w/w % crystalline silica. These results apply globally to any industry where workers are exposed to dust generated from the fabrication of materials containing crystalline silica. Our aim is that future policy development in workplace health and safety will consider the crystalline silica content of natural materials, as well as other synthetic stones (not just engineered stone).

Natural and synthetic stones are mineralogically diverse, so rather than presenting an average value for the crystalline silica content of each stone product, we present the range of possible values. Underestimating the crystalline silica content of a rock poses a health risk, so regulators stand to gain more by reporting the range of measured values in a specific product, or the range of values for a specific type of natural or synthetic stone.

### 2. CRYSTALLINE SILICA IN NATURAL DIMENSION STONE

Dimension stone is natural rock that can be fabricated into shaped stone as a commercial product. It does not include crushed and broken rocks such as aggregates and chemical raw materials (Revuelta 2021; ASTM International 2023). Ornamental dimension stones are commercially classified as 'granite', 'marble', 'limestone', 'quartz-based dimension stone', 'slate', or 'other' (ASTM International 2023) (Table 3). Of these categories, only 'granite' and 'marble' can be polished to create a highly reflective surface, making them equivalent

products to engineered stone countertops. Despite the availability and affordability of engineered stone since the proliferation of manufacturing plants to produce engineered stone slabs from 1979 onwards (Breton 2013), the global production of dimension stone has more than doubled over the last two decades (Figure 1).

Please Insert Table 3.

Please Insert Figure 1.

Given the conflicting scientific and commercial definitions of 'granite' (Table 3, Figure 2), it was necessary to review what rock types are commercially sold as 'granite' dimension stone prior to estimating their crystalline silica content. The conflict between the scientific and commercial definition of granite is perhaps best demonstrated as a pie chart (Figure 3), which summarises our work to classify a catalogue of commercial granite dimension stones (International Granites 2024) using the correct scientific nomenclature. The data that were available on the International Granites (2024) catalogue contained 366 dimension stone products across 25 different countries rock types, where appropriate data were available to assign a correct scientific name (Supplementary File 2). These data show that while 24% of commercial 'granites' are granite sensu stricto, the remainder comprises gneisses and migmatites (37%), granulites and charnockites (12%), silica-saturated alkaline rocks (9%), basic rocks (7%), and anorthosites (4%). Less common rock types (~1%) included metaconglomerates, silica-saturated intermediate rocks, tonalites, foidolite, pegmatites, granodiorite, aplite, igneous breccia, and mylonite.

In the scientific literature, coarse-grained igneous and metamorphic rocks are classified on the relative proportion of silicate minerals in a rock. Plutonic igneous rocks are classified based on the relative proportion of quartz, alkali feldspar, plagioclase feldspar, and feldspathoid (QAPF plot), as well as mafic minerals (M' index), so calculating the range of crystalline silica contents in plutonic and charnockitic rocks is straightforward (and a guide for readers to do this type of calculation is provided in Supplementary File 3). Following this approach, what a geologist will recognise as 'granite' sensu stricto, will contain anywhere between 16 and 57 vol. % crystalline silica.

The range of crystalline silica contents of the 43 varieties of plutonic igneous rocks (any of which can be used as natural countertops) is provided in Supplementary File 4. The range of crystalline silica contents are also summarised in Figure 2. While we have not calculated the range of crystalline silica content for volcanic rocks, their plutonic equivalents should serve as maximum values for crystalline silica content. The crystalline silica content of ultramafic cumulates was calculated assuming 90-100 vol.% mafic minerals and a range of crystalline silica contents equivalent to the field for gabbro (0-5 vol.%) (Le Maitre 2018).

The only igneous dimension stones of commercial significance that cannot be quantified using the QAPF method are pegmatitic rocks. Pegmatites are coarse-grained igneous rocks with crystals >2.5 cm (Le Maitre 2018). Following the International Union of Geological Sciences guidelines, we suggest that pegmatites be classified according to their petrology on a QAPF plot. Some lens-shaped pegmatites can contain cores of massive quartz >100 m in

length (Müller et al., 2021), so it is theoretically possible to have igneous rocks containing 100% crystalline silica on the scale of fabricated dimension stone slabs.

Metamorphic rocks are classified according to their mineralogy and texture, which requires a different approach to calculate their crystalline silica content. The crystalline silica content of a metamorphic rock depends on the volume of silica in the protolith (the precursor rock, prior to metamorphism), the impact of chemical reactions with increasing metamorphic grade, and the addition of silica from quartz veins, or silicification. Our global compilation (Supplementary File 2) reveals that the dominant siliceous metamorphic rocks of commercial significance in the "granite group" are gneiss, migmatite, granulite, charnockite, and metaconglomerate.

During metamorphism, mineral reactions can either consume or produce quartz (e.g., Whitney et al., 1996). For example, the crystalline silica content of a mudstone increases to ~28 vol.% quartz at 350-400°C and 0.8-1 GPa and increases further to ~47% quartz at 550-600°C and 1.6-1.9 GPa during blueschist-grade metamorphism (Spandler et al., 2003).

Traditionally, schists are defined as containing 50-100% platy (e.g., mica) or acicular minerals (e.g., hornblende) showing elongate parallel alignment (Ashton et al., 1990). Given the overlap with distinguishing between schistose and gneissose textures, it has been suggested that schist should be more loosely defined as containing 40-100% platy and acicular minerals (Feininger 1991). This second definition is supported by an X-ray diffraction study of five quartz mica schist samples from the same mine, containing 40-60 vol.% quartz (Zhang et al., 2011). Therefore, schists likely contain 0-60 vol.% quartz.

To characterise the crystalline silica content of high-grade metamorphic rocks with a range of protoliths, we combine gneisses and migmatites into the same category. To be consistent with our definitions, gneiss is a metamorphic rock with compositional layering containing 0-60% platy and acicular minerals (Feininger 1991). Published X-ray diffraction analyses of gneiss range from 3-53 vol% quartz (Ray et al., 2015; Singh and Murthy 2016; Cavallo and Dino 2022). Migmatites are rocks that preserve evidence of partial melting of the crust (Yakymchuk 2021). Migmatites may contain unmelted portions of rock (paleosomes), as well as partially molten rock (neosome). The neosome comprises layers of partial melt rich in feldspar and quartz (leucosomes) and dark residual minerals (melanosomes). X-ray diffraction analyses of migmatite aggregates from a quarry in Rio de Janeiro showed that a paleosome containing 28 vol.% quartz melted to produce leucosomes with 24 vol.% quartz and melanosomes with 10 vol.% quartz (Trotta et al., 2021). Therefore, the quartz content of a migmatite is a function of the quartz in the parental gneiss. Therefore, gneiss and migmatite likely contain 0-60 vol.% crystalline silica.

Mylonites were documented as a "granite-group" rock type in Supplementary File 2. Published measurements of quartz in mylonitic gneiss range from ~40-~50 vol.% (Wilson et al., 2022). Given the range of protoliths for mylonite, we suggest that mylonites probably contain the same range of quartz contents as gneiss (0-60 vol.%) but may contain additional silicification.

Granulites and charnockites represent 12% of the commercial "granite-group" dimension stones analysed in Supplementary File 2. However, granulite-facies metamorphism is

relatively rare, occurring at high temperatures (~700-1000°C), often in CO<sub>2</sub>-rich environments (Frost and Frost 1987). Depending on the protolith, and fluids present during metamorphism, this can produce either mafic, intermediate, or felsic granulites. X-ray diffraction values are reported for mafic granulites (0-17 vol.% quartz), intermediate granulites/enderbitic gneiss (21-47 vol.% quartz), and felsic granulites/charnockitic gneisses (18-34 vol.% quartz)(Ray et al., 2015). There is debate as to whether charnockitic rocks – containing orthopyroxene or fayalite + quartz – are formed by igneous or metamorphic processes (Le Maitre 2018; Streckeisen et al., 1976). In igneous petrology, they can be classified by a modification of the quartz-alkali feldspar-plagioclase feldspar (QAP) ternary plot, where 'A' represents perthite, mesoperthite is distributed evenly between 'A' and 'P', and 'P' represents antiperthite (Le Maitre 2008). However, no estimates for the average contents of mafic minerals (M) are provided. Measured XRD values for M' are 3-14 vol.% for felsic charnockites, 9-24 vol.% for intermediate charnockites, and 26-70 vol.% for mafic charnockites (Ray et al., 2015), commensurate with the range of the M' index to classify typical felsic (M' = 0-25), intermediate (M' = 10-50), and mafic (M' = 25-65) rocks. Using modelled values for the modified QAP ternary plot for charnockitic rocks (Supplementary File 4) and the M' index for silica-saturated felsic, intermediate, and basic rocks (Le Maitre 2018), we calculate mafic granulites/mafic charnockites contain 0-15 vol% crystalline silica, intermediate granulites/mafic charnockites contain 5-54 vol% crystalline silica, and felsic granulites/felsic charnockites contain 8-60 vol% crystalline silica. While cristobalite is preserved in some granulite-facies rocks, it is uncommon and volumetrically insignificant (Darling et al., 1997).

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A detailed petrographic study of a greenschist-facies polymictic metaconglomerate (Etheridge and Vernon 1981) reported that the mineralogy of the matrix ranged from nearly pure quartz to feldspar rich, or mica-rich varieties. Therefore, the matrix of a metaconglomerate can range from 0-100 vol.% crystalline silica. The same study (Etheridge and Vernon 1981) documented crystalline silica in metamorphosed clasts of metadacite (0-35 vol.% crystalline silica), metashale (10-30 vol.% crystalline silica), metasandstone (~70 vol.% crystalline silica) and feldspathic tuff (10-20 vol.% crystalline silica). Therefore, the quartz content of a metaconglomerate could range from low silica (clasts of basic igneous rock in a feldspar, mica-rich matrix), but is more likely to tend towards a high quartz content. The most quartz-rich varieties would consist of quartz pebbles in a quartz matrix: mineralogically equivalent to quartzite, but with larger clasts.

## 2.2 Crystalline silica content of 'limestone' dimension stone products (0-5 vol. %)

Limestones are predominantly made from calcareous sedimentary grains with calcareous cement (e.g., calcite and/or aragonite). Crystalline silica can either be detrital or form during burial diagenesis (Molenaar and de Jong 1987). Limestones and dolostones typically contain <5 vol.% impurities (Blatt and Tracey 1996), meaning that most limestones and dolostones typically contain 0-5 vol.% crystalline silica. It should be noted that clastic rocks containing carbonate grains or carbonate cement are scientifically classified as sandstone, not limestone. On the scale of a mine, limestones can be interbedded with siliciclastic rocks, which may result in elevated values of crystalline silica e.g., up to 45 vol.% crystalline silica measured in 'siliceous limestone aggregates' (Abd-Elssamd et al., 2020).

317 2.3 Crystalline silica content of 'marble' dimension stone products (0-5 vol. %) 318 Limestones typically contain <5 vol.% crystalline silica – so theoretically, their metamorphic 319 equivalents also contain <5 vol.% crystalline silica. Marble quarries used to supply dimension stone are reported to contain "minor", or <4 vol.% quartz (Yavuz et al., 2005). Calcite-320 321 dominated marbles typically contain more quartz than dolomitic marbles, as quartz and 322 dolomite metamorphose to form tremolite (Melezhik et al., 200) or other magnesium-323 silicate minerals. 324 325 2.4 Crystalline silica content of 'quartz-based' dimension stone products (0-100 vol. %) 326 Sandstones comprise sand-sized clasts in a cement matrix. Clasts are predominantly quartz 327 grains, feldspar grains, or rock fragments. Average sandstone contains ~66% quartz clasts 328 (Blatt 1967). These grains may be cemented by a matrix of silica, carbonate, iron oxides, clay, 329 zeolite, or albite. Therefore, sandstones may contain 0-100% vol.% crystalline silica. 330 Quartzite is either classified as metamorphosed sandstone with 80-100 vol.% crystalline 331 silica (Robertson 1999), or 90-100 vol.% crystalline silica (Frost and Frost 2014). 332 2.5 Crystalline silica content of 'slate' dimension stone products (7-88 vol. %) 333 334 A comprehensive review of the mineralogy of roofing slates from 12 countries shows that 335 quartz in slate ranges from 7-55 vol.% crystalline silica (Cárdenes et al., 2014). As the 336 composition of shale varies from siliceous to argillaceous, the crystalline silica content of 337 shale is highly variable, with a range of 10-88 vol.% crystalline silica (Rexer et al., 2014; 338 Xiang-Rong et al., 2018; Zhu et al., 2022).

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## 2.6 Addition of crystalline silica from quartz veins and metasomatism

As fluids are liberated from hydrous silicate minerals during metamorphism, the likelihood of quartz veining and local silicification increases (Terabayashi et al., 2010), especially in more permeable lithologies. For example, siliceous fluids liberated from metamorphism in an accretionary prism increased the crystalline silica content from <3 vol.% quartz veins in low-grade (prehnite-pumpellyite facies) rocks to ~30 vol.% quartz veins in greenschist-facies rocks (Breeding and Ague 2002).

To report the crystalline silica value of a metamorphic rock at the slab or deposit scale, we suggest reporting the vol.% of quartz veining in addition to the crystalline silica content of the metamorphic substrate. For example, in a dimension stone mine where a gneiss (0-60 vol. % crystalline silica) is overprinted by quartz veins (ranging from 5-10 vol.% over the outcrop), the variation at the deposit scale should be reported as 5-70 vol.% crystalline silica.

## 2.7 Other possible natural threshold values for crystalline silica

Figure 2 shows that "granite benchtops" *sensu lato*, range from crystalline-silica free varieties (e.g., foidolite), to 100% crystalline silica (e.g., quartz cores in silica-oversaturated acidic pegmatites). Self-reported analyses in commercial granite products range from below detection to 41 vol.% crystalline silica (n = 70, Supplementary File 2), commensurate with an independent petrological study of granite-group dimension stone slabs containing 11-44 vol.% crystalline silica (n = 10) Johnson et al., 2012) determined by point-counting minerals with a petrographic microscope.

We propose that other natural thresholds may be informative for regulators, such as the average volume of quartz in the continental crust (12 vol.% crystalline silica) (Ronov and Yaroshevsky 2016), the maximum volume of quartz in granite *sensu stricto* (57 vol.% crystalline silica, Supplementary File 3), or the volume of quartz in average wind-blown dust called loess (45-55 vol.% crystalline silica) (Pye 1991). Wind-blown dust contains RCS, as >50% of grains are 2-63 µm in size (Pye 1991). The public health literature generally agrees that inhalation of aged dusts is less toxic than those which are recently fractured, and that the reactivity of wind-blown natural dusts may be modified by the presence of clay and other minerals (IARC 2012). However, incidences of silicosis have been attributed to exposure to RCS from loess (Norboo et al., 1991). While we provide these alternative natural thresholds, we advocate for policy thresholds determined by data from clinical trials, in vivo, or in vitro studies instead of natural thresholds in the first instance.

### 3. CRYSTALLINE SILICA IN SYNTHETIC STONE

Here, we describe synthetic stone as any man-made stone product. This encompasses engineered stone products (see definition in Table 1), as well as synthetic products that are not attributed to the increase of accelerated silicosis cases in the last decade, such as resinbased stone products, terrazzo, porcelain, concrete and cement, and bricks.

## 3.1 Crystalline silica content of engineered stone products (0-91 vol. %)

Engineered stone is manufactured by mixing particles of one or more materials (e.g., minerals, glass) with a binding agent (e.g., resin, cement) before curing the product at either room temperature or up to 500°C. Patents describe a bimodal grain size of aggregates in engineered stone products, comprising coarse aggregates (500 microns to 10 cm) in a matrix

supported by fine particles typically  $^{\sim}20~\mu m$  in diameter (Grzeskowiak and Davis 2015; Lee et al., 2019; Li 2021; Adams and Caselli 2024).

Theoretically, the minimum crystalline silica content of engineered stone is 0 vol.% crystalline silica, assuming it is manufactured without crystalline silica particles (e.g., particles of glass (Caeserstone 2024a; Quantum Zero 2024; YDL Stone 2024), amorphous minerals (Lavistone 2024), or carbonate minerals (Silva et al., 2017; Samad et al., 2021). Some aggregates contain mixtures of amorphous phases and crystalline silica (e.g., YDL Stone 2023), or mixtures of amorphous minerals and carbonate minerals (Lavistone 2024). Another popular crystalline silica-free alternative for countertops are solid surface composites, which contain ~70 vol.% powdered alumina trihydrate (gibbsite), bound in an acrylic polymer matrix with binders, pigments, and trace metals (Mandler et al., 2023). These products do not report crystalline silica in safety data sheets (Du Pont 2023). Many of these mixtures meet the technical requirements of the current Australian ban on engineered stone with >1% crystalline silica and have been marketed as "zero silica", "silica free" or "crystalline silica free" benchtops.

However, since most of these "zero silica" products are new to the market, most available data on the silica content of engineered stone relates to engineered stone products that were developed before the Australian ban on the import and manufacture of engineered stone with >1% crystalline silica. Some of this information includes what was advertised as 'low silica' benchtops, for instance where the Australian Government was initially considering implementing a ban on products with >40% crystalline silica. Safety data sheets

for some of these 'low-silica' kitchen countertops report crystalline silica values of up to 28 vol.% (Caeserstone 2024b; CDK Stone 2021; YDL Porcelain 2023).

We are also unsure if new "zero silica" products are being used outside of Australia (e.g. if traditional high crystalline silica benchtops continue to be sold in other countries). We have therefore reported the available range of crystalline silica contents of all engineered stone products. For example, the crystalline silica contents of 25 engineered stone products from 6 suppliers determined by X-ray diffraction (XRD) Rietveld refinement show that typical engineered stone ranges from 58-91 vol.% crystalline silica, with 8-15 vol.% resin (Kumarasamy et al., 2022). This work showed that self-reported data in safety data sheets for engineered stone can be inaccurate (Kumarasamy et al., 2022). A second study of crystalline silica in synthetic stone using XRD Rietveld refinement presents values of 0-90 vol.% crystalline silica from 12 'resin-artificial stones' (including solid surface composites) (Hall et al., 2021). Fernández Rodríguez et al., (2013) report some statistics (not individual analyses) from 91 samples of engineered stone measured using Rietveld refinement. They report that 67% of engineered stone samples contain > 90 vol.% quartz, and 73% of samples contain <1 vol.% cristobalite, with 19% of samples containing > 10 vol.% of cristobalite.

3.2 Crystalline silica content of porcelain products, ceramics and bricks (1-75 vol. %)

Porcelain stone benchtops are now marketed as a popular lower-silica alternative to engineered stone. Most porcelain products are predominantly made from a mixture of fine-grained (typically <63 µm) quartz and/or flint\* particles (Carty and Senapati 1998), feldspar,

<sup>\*</sup>Flint is a rock made of microcrystalline silica, which can contain quartz, cristobalite, tridymite, and/or opal, depending on the diagenetic history of the rock (Knauth 1994).

and clay. Varying proportions of these components create different porcelain stoneware products (e.g., See Figure 2 in Zanelli et al., 2011). Sintering quartz, feldspar, and clay at high temperatures transform their composition into quartz, feldspar, mullite, and glass. The proportion of quartz in porcelain decreases with increasing firing temperature (1000-1250°C), as the quartz and feldspar are consumed to form a vitreous phase (Zanelli et al., 2011). Estimates of crystalline silica in porcelain products using XRD Rietveld refinement range from 7-29 vol.% crystalline silica (n = 36) (Dondi et al., 1999; Amigó et al., 2004; Hutchings et al., 2006; Zanelli et al., 2011). An unsintered 'ceramic' countertop alternative was found to contain 1 vol.% quartz (Hall et al., 2021). Modern ceramics made using shorter firing schedules and lower firing temperatures favour the production of quartz, so cristobalite is typically absent (Carty and Senapati 1998). Archaeological samples of porcelain contained higher crystalline silica contents than modern stoneware (e.g. up to 44 vol.% crystalline silica in Spanish porcelain made between 1760 and 1783 (Aza et al., 2004)).

Safety data sheets for thin set mortar products used to cement porcelain tiles report a range of 25-100 vol.% crystalline silica (Laticrete 2015; Mapei 2022; 2023; Custom Building Products 2012; 2015; 2010; Adelaide Brighton Cement 2020). However, bulk dust measured from tuckpointing residue contained only 4-5 vol.% crystalline silica (Lofgren 1993). Excluding the upper value of 100 vol.% crystalline silica (Custom Building Products 2010), we suggest thin set mortars typically contain 4-75 vol.% crystalline silica.

Bricks are made from clays containing ~32-58 vol.% quartz (Dunham 1992; Sims et al., 2006), but the value of crystalline silica decreases on firing as quartz is transformed into a vitreous phase. Safety data sheets of clay bricks and clay paver self-report values of 5-75 vol.%

crystalline silica (General Shale Brick 2015; ACME Brick Company 2019; US Brick 2021; Belden Brick Company 2022; CSR Building Products 2023).

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3.3 Crystalline silica content of cement and concrete products (0-88 vol. %)

Concrete is a mixture of cement, fine aggregate, and coarse aggregate. The grade of concrete (e.g., ordinary concrete, standard concrete, and high strength concrete) is determined by varying these components (Bureau of Indian Standards 2007). Portland cement nominally contains 0 vol.% crystalline silica, as it is made from clinker comprising polymorphs of alite (Ca<sub>3</sub>SiO<sub>5</sub>), belite (Ca<sub>2</sub>SiO<sub>4</sub>), ferrite (Ca<sub>4</sub>Al<sub>2</sub>Fe<sub>2</sub>O<sub>10</sub>), aluminate (Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>), and calcium oxide (Torre et al., 2001). However, siliceous additives may be included in some cement mixtures (Bureau of Indian Standards 2007), which include fly ash (56-66% SiO<sub>2</sub>; 2-5 vol.% quartz (Matsunaga et al., 2002), silica fume (up to 100% SiO<sub>2</sub>; 0.2-9 vol.% quartz (Fletcher et al., 1994; Mikhail and Turcotte 1997), rice husk ash (92-97% SiO<sub>2</sub> (Shen et al., 2011); <5-87 vol.% quartz and cristobalite). Typical anhydrous cement contains ~1 vol.% quartz (Walenta and Füllmann 2004). Lower grades of concrete have the greatest potential to contain crystalline silica, as the ratio of cement to aggregate increases with the grade of concrete (Torre et al., 2001). Concrete typically contains 60-80 vol.% aggregate, comprising coarse and fine aggregates (Linch 2002). Typical aggregates used in concrete include sands, and gravels, as well as crushed unweathered granites, dolerites, sandstones, and some limestone (Fookes and Walker 2010). The maximum crystalline silica value of concrete is 88 wt.% quartz, assuming low-grade (grade M5) concrete containing a mixture of 50 kg cement (containing 1 vol.% quartz), to 800 kg dry quartz aggregate (sand and pebbles), and 60 kg water (excluding the addition of siliceous additives) (Bureau of Indian Standards 2007). XRD measurements of fine recycled aggregates (0-4 mm) made from concrete or construction

and demolition waste report 48-72 vol.% quartz (Netherlands, n = 3) (Nedeljković et al., 2021) and 43-86 vol% quartz (Portugal, n=10) (Rodrigues et al., 2013). These values are commensurate with safety data sheets (e.g., Cemex 2017; Hanson Construction Materials 2020) which report 0-85 vol.% quartz in premixed concrete, depending on the type of aggregates used.

Terrazzo is a mixture of aggregates bound by either Portland cement or epoxy resin, poured *in situ* onto existing surfaces (e.g., flooring and stairs), or prepared as tiles. The resin used to bind aggregates can contain 0.1-1 vol.% crystalline silica (Terrazzo and Marble Supply 2021; Silka 2023). Aggregates used in terrazzo floors can vary widely. While marble is the most common, other aggregates include onyx, travertine, serpentine, quartz sand, granite, quartzite, mother of pearl, polymer, glass, ceramic, cork, and slag (Murray 1967; Kunio and Kiyoshi 1992; Arnold 2012; Seok 2013; Reveulta 2021). The composition of terrazzo floors ranges from 0-66 vol.% crystalline silica in patents of resin-based terrazzo (Arnold 2012; Seok 2013) and 40-50 vol.% crystalline silica in patent for precast cement-based terrazzo tiles (Murray 1967). Theoretically, the upper limit of crystalline silica could exceed these values if large slabs of quartzite or other quartz-rich rocks were incorporated in a palladiana-style terrazzo layout (e.g., Reveulta 2021).

## 4. REDUCING EXPOSURE TO RESPIRABLE CRYSTALLINE SILICA DURING FABRICATION

The toxicity of any substance is first determined by the dose – the duration and intensity of exposure – as well as the physical and chemical characteristics of both the material and the exposure route (Plumlee et al., 2006). The duration of exposure is controlled by how many hours a worker spends fabricating stone, over their career. Here, we briefly review the

factors controlling the intensity of exposure during the fabrication of natural and synthetic stone in the workplace.

4.1 Reducing crystalline silica content of mineral dust during fabrication of stone products

Few experimental data exist where both the stone substrate and mineral dust produced

have been measured. Figure 4 presents available experimental data to demonstrate that the

crystalline silica content of dust produced during cutting and polishing stone is controlled by

the crystalline silica content of natural and synthetic stone slabs, with minimal contribution

from the grinding tool in typical workplaces.

Mineral dusts generally increase in toxicity as the crystalline silica content of rocks increases — a trend that is exemplified by data from autopsies of workers with advanced lung diseases (See Figure 3 in Nagelschmidt 1960). Nagelschmidt (1960) observed that miners exposed to mineral dust with <0.1 vol.% crystalline silica developed quartz-free massive fibrosis after ~70 grams of dust accumulated in both lungs. In contrast, quartz miners exposed to mineral dust with 20–60 wt.% silica developed silicosis post-exposure with a tenth or less of the total dust exposure (4 – 7.4 grams of dust in both lungs). They noted that accelerated silicosis occurred in workers exposed to dust with >30 vol.% crystalline silica. These observations are largely reflected in modern exposure limits for crystalline silica, which have an 8-hour time-weighted average (TWA) of 0.05 mg/m³ compared to an 8-hour TWA of 10 mg/ m³ for low-toxicity dusts (Safe Work Australia 2024c).

Interestingly, recent research has shown that other silicate minerals, such as micas and feldspars can also induce cytotoxicity (Grytting et al., 2022) – this is an important finding,

both for the processing of natural stones (where most igneous rocks contain different proportions of quartz, micas and feldspars), as well as engineered stone (e.g., if mica and feldspar were used as substitutes for quartz).

Please Insert Figure 4.

### 4.1.1 Reducing crystalline silica in engineered stone

If we assume that the amount of crystalline silica in a material is equivalent to the crystalline silica in dust generated from cutting that material, it follows that reducing the amount of crystalline silica in an engineered stone product will reduce worker exposure to RCS. During the Australian Government's deliberations on banning engineered stone products, manufacturers moved to limit the amount of crystalline silica in their products to <40% or <10% between 2023 and 2024. Manufacturers later moved to producing engineered stone with <1% crystalline silica ("zero silica") between 2024 and 2025 to meet the requirements of Australian law. We have therefore calculated the relative difference of potential RCS exposure between the original forms of engineered stone (with crystalline silica contents of 58–91%) to alternative products such as porcelain, "low silica" engineered stone, and "zero silica" engineered stone (Figure 5; Supplementary File 5). These calculations indicate that compared to traditional high-quartz engineered stone, RCS exposure will be reduced by:

- 48–92% when working with porcelain
- 33–73% when working with "low silica" engineered stone products
- 98–100% when working with "zero silica" engineered stone products

Workers who exclusively fabricate new "zero-silica" engineered stone should theoretically not be exposed to minimal RCS when fabricating this material. However, while they may not inhale RCS, they may still be at risk if the aggregates used in these newer products causes harm. The risk associated with the emission of potentially toxic volatile organic compounds from resin (Ramkisson et al., 2022) may also remain with these newer "zero silica" products. Workers will also remain at risk of lung disease over a longer time frame if their workplaces do not add additional mitigation measures to address the overall volume of mineral dust and volatile organic compounds produced by alternative 'crystalline silica-free' products.

Realistically most stone workers will also continue to work with other products such as natural stone and/or porcelain/sintered stone, which, as we have shown typically contain variable amounts of crystalline silica (and almost always >1% crystalline silica) – these materials will therefore continue to be a risk to the health of stone fabricators (as well as workers in other industries such as mining, tunnelling, and construction) without including other control measures (Figure 5).

Please Insert Figure 5.

# 4.2 Controls on the volume fraction of respirable dust produced during fabrication of stone products

The volume of total dust produced – and the proportion of respirable dust – are controlled by the tools used for fabrication, as well as the mechanical properties and composition of the stone substrate. The type of tool used to fabricate stone affects the volume of dust and

RCS produced (Qi and Echt 2016; Weller et al., 2024). The type of stone substrate also affects the volume and proportion of respirable dust emitted during fabrication (Carrieri et al., 2020; Thompson and Qi 2022). Occupational tasks conducted in the vicinity of rock fabrication (e.g., sweeping, brushing, loading materials, washing floors, etc.) also expose workers to RCS (Linch 2002). The sharpness or dullness of a tool also influences the particle size of mineral dust. A study of limestone fabrication with a metal pick found that as the pick became more blunt, the particle size slightly decreased, increasing the volume of respirable dust produced (Slouka et al., 2022). The same trend was observed using a hammer drill on concrete (Carty et al., 2017). Harder rocks (controlled by the modal mineralogy, size, and shape of grains, and bond strength between grains in a rock) wear tools faster than softer rocks (Ersoy et al., 2005). Typically, tools wear faster as the silica content of a rock increases (Ersoy and Waller 1995). Therefore, the volume of RCS dust generated from the fabrication of natural and synthetic stone slabs is primarily controlled by the crystalline silica content of the slab, the method of fabrication used, and environmental conditions at the site of fabrication.

4.3 Mitigating human exposure to respirable crystalline silica during stone fabrication

Control measures can be used to reduce exposure to RCS in workplaces involved with the fabrication of natural or synthetic stone. We have summarised the relative efficacy of the different solutions to reduce RCS and mineral dust exposure by considering four components: (a) reducing the amount of crystalline silica in the materials being fabricated (discussed in section 4.1); (b) using water to suppress dust during fabrication; (c) using local exhaust ventilation (LEV) on cutting and polishing equipment; and (d) wearing suitable personal protective equipment such as a face mask or respirator (Figure 5). Each of these

four components reduces worker exposure to RCS by different amounts, but exposure to the amount of mineral dust generated from the materials requires wet cutting, local exhaust ventilation, and/or wearing suitable personal protective equipment.

### 4.3.1 Using water to suppress dust during fabrication

Water is commonly used to suppress dust generated during stone fabrication. Previous work has shown that wet cutting reduces exposure to RCS by 89% when using a circular saw without local exhaust ventilation (Cooper et al., 2015). Similarly, sheet-flow wetting has been shown to reduce exposure to RCS by 68% when using a SiC grinding wheel with LEV, or by 52% with a blade without an LEV shroud (Johnson et al., 2017). The use of water is also thought to reduce the toxicity of silica dust and reducing the activity of free radicals on newly generated particle surfaces (particle 'ageing') (Meldrum and Howden 2002). The ageing process is unlikely to markedly alleviate the enhanced reactivity of freshly cut surfaces in the seconds between cutting and inhalation (Meldrum and Howden 2002), but should theoretically reduce the reactivity of dusts that might accumulate after wet cutting. Overall, the use of water-based dust suppression reduces RCS by 52-89% and the exposure to mineral dust by 52-89% (Figure 5).

### 4.3.2 Using local exhaust ventilation (LEV)

Local exhaust ventilation systems are commonly used to reduce worker exposure to dust generated from fabrication. Existing work has shown that the use of LEV reduced RCS exposure by (a) 26% when dry cutting with a blade (Johnson et al., 2017); (b) 85% when dry grinding (Johnson et al., 2017); (c) 99% while wet cutting with a circular saw (Cooper et al., 2015), and (d) ~95% when wet grinding using sheet flow wetting (Johnson et al., 2017).

Overall, the use of LEV systems will likely reduce RCS and mineral dust exposure by 26–85%, which can increase to ~95–99% when combined with water suppression (Cooper et al., 2015; Johnson et al., 2017) (Figure 5). However, the use of LEV systems may not effectively remove particles if the LEV design is poor, the work area is larger than the LEV coverage and routine maintenance of the LEV is lacking (cf. Burton, 2013).

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### 4.3.3 Respiratory Protective Equipment

It is common knowledge that exposure to RCS and mineral dusts can also be limited by wearing personal respiratory protective equipment. Respirators work by acting as a barrier, to reduce the volume of dust that a worker may inhale. The amount of protection depends on the grading of the equipment. For example, in Europe, respirators are classified according to the European standard EN 149:2001+A12009 which has three classes of filtering facepieces (FFP1, FFP2 and FFP3). FFP1 is the lowest grade and filters 80% of particles that are 0.3 micron particles and above. FFP2 masks and FFP3 are higher grade filters that limit a minimum of 94% to 99% of particles respectively. Similar grades of respirators are available in other countries and are governed by appropriate standards and government regulators (e.g., in the USA, respirators are classified according to the National Institute for Occupational Safety and Health (NIOSH) standard, where broadly equivalent respirator classes exist. For instance, the NIOSH N95 respirator is broadly equivalent to the EU FFP2 standard). However, the efficacy of respiratory protective equipment is compromised without training, correct fitting and leakage (e.g., due to the presence of facial hair), maintenance, and continuous usage (e.g., Janssen et al., 2014). Experimental work has shown that RCS exposure can be reduced by ~92.3% when cutting sandstone with a saw, and factoring in a maximum internal leakage ratio of 6.7% for RCS and a FFP3 mask (Stacey et al.,

2020). We therefore propose that RCS and mineral dust exposure can be reduced by 87–99% using appropriate PPE (i.e. at least a FFP2 or N95 mask).

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### 5. TOXICITY OF SILICA DUST PRODUCED DURING FABRICATION OF STONE SLABS

At the molecular scale, the mechanisms driving the toxicity of RCS are counterintuitive. It is well established that the act of fabrication (i.e., cutting, grinding, milling, or polishing) crystalline silica-bearing stone slabs and creating RCS enhances its toxicity. However, the act of grinding quartz creates a zone of highly disordered – i.e., non-crystalline or poorlycrystalline – silica (20-800 nm in thickness), sometimes coated in a thin film of amorphous silica (~20-30 nm in thickness) (Gibb et al., 1953; Šolc 1966; Battaglia et al., 1990; Balek et al., 1995; Smith 2002). The concept of a poorly crystalline surface coating on respirable crystalline quartz is paradoxical because non-crystalline (i.e., amorphous) silica typically has higher permissible exposure limits than crystalline silica (Safe Work Australia 2024c) and it is not considered carcinogenic (due to inadequate evidence) (IARC 1997). It is possible that highly disordered silica may concentrate at the edges and corners of particles, rather than form a complete coating, depending on the method of fabrication (Steinike et al., 1982) (Figure 6). After fabrication (breaking of Si-O bonds), the surface of quartz can swell to form a thin amorphous film if submerged in water (pH 7) for > 17 days (Li et al., 2004). These conditions are comparable to extracellular lung fluids (pH 7.4) and for macrophage intracellular fluids (pH 3-6.9) (Plumlee et al., 2006).

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Mechanical fracture of silica polymorphs breaks silicon-oxygen bonds to form highly reactive species through either: (1) homolytic cleavage, which creates surface radicals; or (2)

heterolytic cleavage to form Si<sup>+</sup> and O<sup>-</sup>, which creates polarity (Fubini and Areán 1999)

(Figure 6). Recent studies propose that silica toxicity is caused by the molecular structure of the highly disordered surface in crystalline silica particles (Turci et al., 2016; Brinker et al., 2020; Leinardi et al., 2020; Pavan et al., 2020; 2022); the cytotoxicity of the silica surface is attributed to either reservoirs of reactive oxygen species, including the opening of distorted or highly strained siloxane bridges, or from the local density of nearly-free silanols (a specific population of weakly interacting silanols that are a key surface feature of crystalline silica polymorphs which govern that influence the body's' recognition and reaction to crystalline silica) (Figure 6). While there is contention around the specific structure of silica groups at the surface of fabricated crystalline silica particles, researchers agree that the disordered surface chemistry of freshly fabricated crystalline silica particles causes the enhanced toxicity of RCS (Turci et al., 2016; Brinker et al., 2020; Leinardi et al., 2020; Pavan et al., 2020).

The complexity of RCS is compounded by the variable silica hazard (Donaldson and Borm 1998; Pavan and Fubini 2017), meaning that the toxicity of a particle can vary with the provenance of the crystalline silica particle, as well as its interaction with other materials in the respirable dust. The surface characteristics and toxicity of quartz relative to other silica polymorphs have also in the past been attributed to its piezoelectricity (Williamson et al., 2001).

Please insert Figure 6.

## 6. POTENTIAL HAZARDS FROM NEW 'CRYSTALLINE SILICA-FREE' PRODUCTS

Following the Australian ban on the manufacture, supply, processing, and installation of engineered stone with > 1w/w% crystalline silica (Safe Work Australia 2024a), a new range of 'crystalline silica-free' engineered stone products have emerged. Safety data sheets describe these new materials as aggregates of "recycled glass" (Caeserstone 2024a; Quantum Zero 2024; YDL Stone 2024), or "amorphous minerals" (Lavistone 2024) in resin, containing <1 w/w% crystalline silica. These are new materials, so few historical data on incidences of lung disease associated with their fabrication are available.

The chemical variability and potential for co-exposures from respirable "recycled glass" and "amorphous minerals" in new crystalline silica-free engineered stone products make the toxicity of these materials difficult to predict. For example, commercial glass products range in chemistry from vitreous silica (100 wt% SiO<sub>2</sub>) to glass bottles (~74 wt% SiO<sub>2</sub>), to electronic sealing (3 wt% SiO<sub>2</sub>, 74 wt% PbO) (Varshneya and Mauro 2019). White recycled glass cullet shows evidence of strained 3-membered siloxane rings (Serbource et al., 2024). Strained siloxane rings undergo homolytic cleavage and hydrolysis to create hydroxyl radicals (Figure 6) (Zhang et al., 2012; Brinker et al., 2020), forming reservoirs of reactive oxygen species. It is thought that these strained siloxane rings are what make respirable pyrogenic silica more toxic than low-temperature amorphous silica dusts (Croissant et al., 2020).

Limited historical data exist on the risks associated with the inhalation of ground recycled glass or ground amorphous silica minerals. The biodurability of <u>crystalline silica</u> enables it to persist in the lung while other minerals are cleared through dissolution or removed by macrophages (Plumlee et al., 2006). However, amorphous silica is considered to have a

relatively low biopersistence, and can be more readily cleared from the lung, limiting its potential for chronic toxicity (particularly compared to crystalline silica). The differential clearance capacity is therefore a critical factor in distinguishing the toxicological profiles of amorphous and crystalline forms of silica (IARC, 2012). It is also worth mentioning the results of a recent study, which investigated the relative cytotoxicity of dusts generated from two samples of "zero silica" engineered stone (Ramkissoon et al., 2025). This study found that the "zero silica" samples generated a lower membranolytic activity compared to dusts generated from traditional engineered stone (although only after the samples were first substantially heated to remove resin). It is also worth noting that the samples containing zero crystalline silica were prepared in a different manner to those containing silica, which potentially influenced the particle size and shape of the material that was examined. Regardless, and what is more concerning is that there have been several studies that have reported high rates of silicosis (in up to 56% of workers) and respiratory impairment after their exposure to "respirable glass clouds of dust" and high fluxes of respirable heavy metals while processing glass bangles and other items in Firozabad, Uttar Pradesh, India (Rastogi et al., 1991; Singh et al., 2023; 2024). These reports raise our concern over the potential for recycled glass being used as a substitute for crystalline silica in new generations of engineered stone, particularly if stone workers perceive they will not develop silicosis or other lung diseases by working with these new materials.

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### 7. SUMMARY

Our study highlights that both natural and synthetic stone can contain significant quantities of crystalline silica, which can pose a significant risk to workers fabricating these materials.

Surprisingly, concrete can contain as much crystalline silica as some quartz-rich engineered stone products. We propose that reporting the range of crystalline silica in heterogeneous materials is more meaningful than the mean. We suggest that regulators propose suitable threshold values for crystalline silica products from the public health literature, rather than natural thresholds where practicable.

The prohibition of engineered stone is likely to prove to be a highly effective method to reduce exposure to RCS in the workplace. However, this measure will not reduce the overall volume of dust produced from working with alternative materials. The use of engineering controls such as water misting and LEV as previously discussed combined with the correct use of respiratory protective devices (including fit testing) will collectively help to further reduce a worker's exposure to RCS.

We highlight that the toxicity of RCS is inherited from a highly disordered silica layer formed during fabrication (cutting, grinding, milling). Therefore, extreme caution should be used when creating synthetic products (such as alternative engineered stone products) from amorphous silica-rich materials. In addition to crystalline silica content, the size of particles generated during fabrication is also a crucial factor in assessing the potential toxicity of materials. Advances in technology mean that our society will continue to create and use new stone products in the future, but the potential health risks associated with fabricating these new materials should be quantified before they are brought to market. Government and regulatory authorities also play an important role in enforcing lower exposure standards

and workplace monitoring to assess existing controls and highlight areas for improvement of controls. **ACKNOWLEDGEMENTS** The work that is presented here was supported by an internal ("AEGIS") grant that was awarded to Dominique Tanner, Lloyd White and Vinod Gopaldasani at the University of Wollongong. The authors thank the editorial team as well as three anonymous reviewers for valuable suggestions that have improved the manuscript. **AUTHOR CONTRIBUTIONS: CRedit** The paper was conceptualised by Dominique Tanner and Lloyd White. Dominique Tanner conducted the formal analysis of data. The original draft was written by all authors. All figures and supplementary files were created by Dominique Tanner and Lloyd White. **COMPETING INTERESTS** The authors declare no competing interests. 

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1216 1217	

### **TABLES**

# Table 1. Definitions of terminology

Crystalline silica (CS):	Silica (SiO <sub>2</sub> ) minerals arranged in a crystal lattice with long-range periodicity. While many varieties of SiO <sub>2</sub> polymorphs exist (Gotze 2012), the most common forms of crystalline silica with industrial applications are quartz, cristobalite, tridymite, and 'tripoli' (microcrystalline quartz) (Berg and Masters 1994).
Dimension stone:	Natural stone products fabricated to specific sizes and shapes (excluding crushed aggregates and raw chemical materials) (see ASTM International 2023).
Engineered stone:	(syn. artificial stone) Artificial slabs of dimension stone made by binding aggregates of rocks, minerals, or synthetic mineral substitutes (e.g., glass, shells), in resin at high temperatures.
Fabrication:	methods used to transform rock into a stone product including cutting, polishing, splitting, grinding, and drilling (see ASTM International 2023).
Low-toxicity dust:	(syn. inert dust, nuisance dust) Poorly soluble, non-fibrous particles <10 µm in diameter which have negligible effects on the body at low levels of exposure, but can cause occupational lung disease if accumulated over time (see Cherrie et al., 2013)
Silica:	The molecule silicon dioxide ( $SiO_2$ ) in any phase. Typically reported as a weight percent oxide ( $SiO_2$ wt%) in analyses of rocks and minerals.
Synthetic stone products:	A broader term encompassing all artificially made solid mineral aggregates with commercial value. This includes engineered stone, solid surface composites, ceramics, mortar, bricks, cement, concrete, and terrazzo.

# **Table 2.** Examples of accelerated silicosis associated with the fabrication of quartz-rich

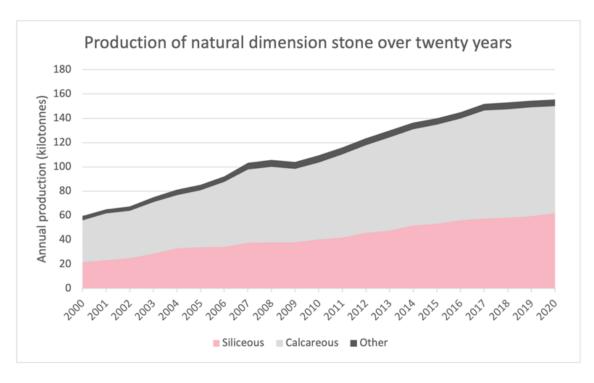
#### materials.

Industry	Stone benchtop community,	Male rock drillers in underground gold
	Victoria, Australia	mine, Jiangxi, China
Number of workers	544	574
screened	(Hoy et al., 2023)	(Tse et al., 2007)
Number of workers	117 (22%)	167 (29%)
diagnosed with	(Hoy et al., 2023)	(Tse et al., 2007)
silicosis		
Average duration of	12 years	5.6 years (working
work in the industry	(Hoy et al., 2023)	10 hours/day)
		(Tse et al., 2007)
Crystalline silica	58-91 vol. %(this study)	~76 vol.%
content of		(Tse et al., 2007)
fabricated material		

# **Table 3.** The geology of dimension stone products

Granite group:	crystalline rocks e.g., granite, gneiss, labradorite, gabbro, basalt
Marble group:	carbonate rocks that can be polished e.g., marble, 'limestone marble', 'onyx marble' and some microcrystalline limestone
Limestone group:	e.g., limestone, coquina, dolomite
Quartz-based dimension stone group:	e.g., sandstone, quartzite
Slate group:	e.g., slate, shale
Other:	e.g., alabaster, serpentine, greenstone, soapstone, schist, travertine

#### 1231 FIGURES



**Figure 1:** Historical production of natural dimension stone from 2000-2020 using data provided in the XXXII Marble and Stone in the World Report (Montani 2021). These data show that the production of siliceous dimension stone (i.e., granite-group and quartz-based dimension stone) has increased from 22 kilotonnes in 2000 to 61 kilotonnes in 2020.

### Abundance of crystalline silica in natural and synthetic rocks

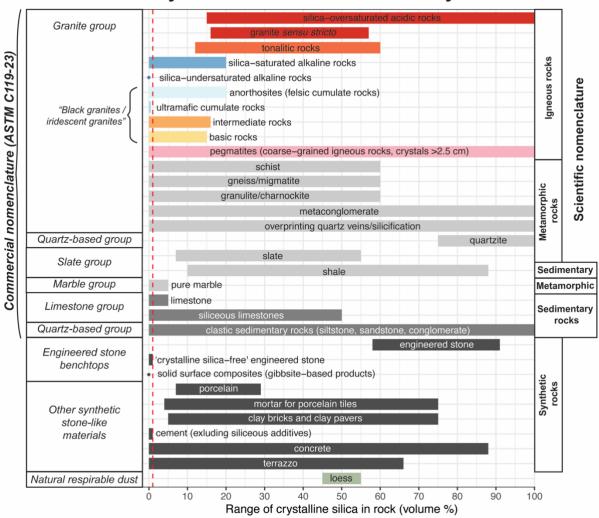


Figure 2. A plot that summarises the range of crystalline silica content of natural rocks and synthetic stone. The range of crystalline silica contents for a given rock type is shown on the x-axis. Commercial classifications of each rock are shown on the left-hand side of the plot, while the right-hand side of the figure groups rocks using their scientific terminology. Silica-oversaturated acidic rocks are shown in red (most quartz-rich), tonalitic rocks are dark orange, silica-saturated alkaline rocks are light orange, intermediate rocks are pale blue, mafic rocks are dark blue, anorthosites are yellow, and silica-undersaturated alkaline rocks are dark blue.

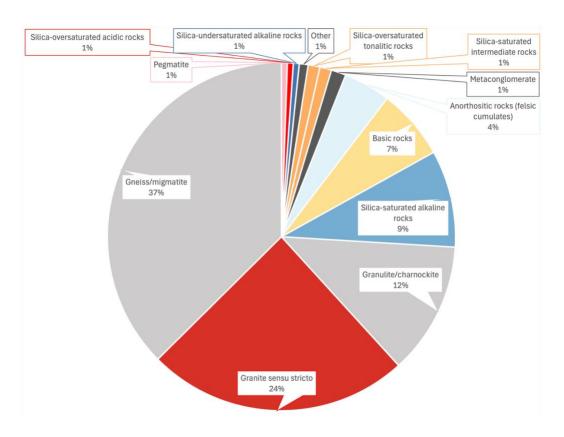


Figure 3: Pie chart showing the results of an analysis of 368 commercial dimension stones used as kitchen countertops that have been marketed or otherwise categorized as "granite". The segments of the pie chart reflect the terminology that a geologist would use to classify these materials using the correct scientific nomenclature. For example, only 24% of materials that are commercially considered to be "granite" are actually granite *sensu stricto*. These results demonstrate how naming conventions can differ, which is an important factor to consider for future policy development around the crystalline silica content of natural stones commonly used for countertops.

#### (orange) and dry polishing (blue) using data from Hall et al. (2021) 90 Respirable crystalline silica generated during fabrication (vol. %) y = 0.89x - 0.614280 $R^2 = 0.9646$ artifical stone artifical stone 70 60 natural 50 artifical stone 0.4574x - 1.6379 30 $R^2 = 0.8317$ 20 natural sandstone 10 "granite" 0

Relationship between CS in bulk material and respirable dust during dry cutting

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Dry cutting

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Dry polishing

**Figure 4:** Plot showing the relationship between the crystalline silica content of mineral dusts produced during controlled experiments of the fabrication of natural rocks and synthetic stone. The values that are shown in orange were produced during the dry cutting of stone using a saw, which approximates a 1:1 relationship between the crystalline silica content of the original material and the resulting dust. The values in blue were produced by dry polishing of stone for 1 hour (dry polishing for 1 hour is highly unusual in industry and the results potentially include abrasive materials generated from ablating the polishing pad).

Crystalline silica content of stone prior to fabrication (vol. %)

----Linear (Dry cutting)

90

..... Linear (Dry polishing)

100

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1272

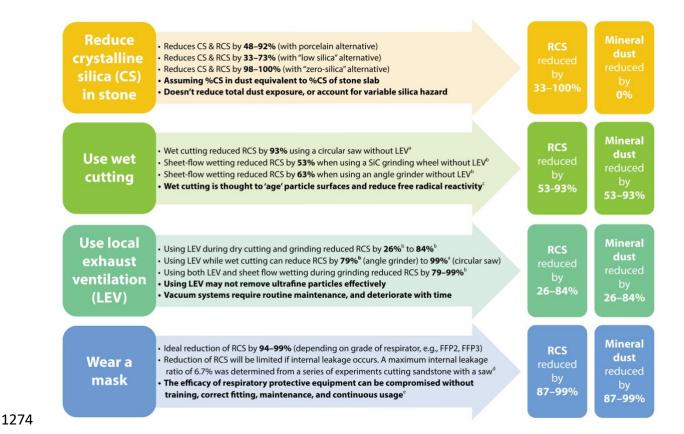


Figure 5: An overview of the relative efficacy of different solutions to reduce respirable crystalline silica (RCS) and mineral dust exposure in stone countertop fabrication, using published empirical and experimental data. The values that are shown for the reduction in crystalline silica in engineered stone reflect the percent differences between the minimum and maximum range of crystalline silica for traditional engineered stone with a high quartz (and/or cristobalite) content compared to the range of crystalline silica expected in porcelain, "low-silica" engineered stone and "zero-silica" engineered stone (Supplementary File 1). The calculations and source of data that were used to create this Figure are available in Supplementary File 5. References: aCooper et al., (2015); bJohnson et al., (2017);

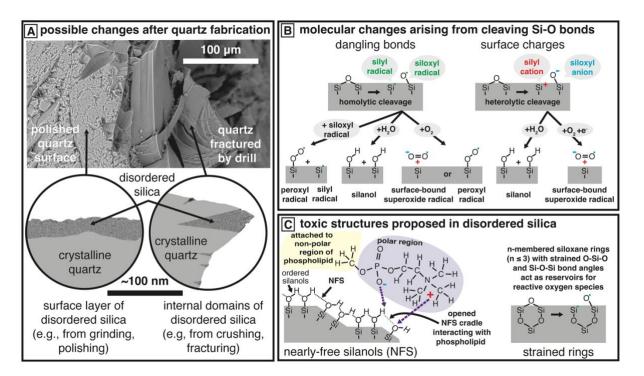


Figure 6: Changes in the mineralogy and surface chemistry of crystalline silica following fabrication. (A) The backscattered electron image (top) shows quartz in a granite benchtop after polishing (top left) and being cut with a drill press (top right). The two schematic diagrams (beneath) depict two possible endmembers of how disordered silica may be distributed in quartz after fabrication (see Steinike et al., 1982) (these deformation styles are not mutually exclusive). (B) Fabrication breaks Si-O bonds at the surface to form dangling bonds or surface charges. These products can react with oxygen or radicals to create more reactive species or react with water to form a layer of silanols (see Bellomo et al., 2023; Fubini 1998 and references therein). (C) Specific molecular structures have been attributed to the toxicity of disordered silica surfaces on respirable crystalline silica (RCS), including (left) nearly-free silanols which might interact with red blood cells containing phospholipids (e.g., 1,2-dioleoyl-sn-glycero-3-phosphocholine) (see Pavan et al., 2020; 2022), and (right)

1300	strained siloxane rings which may act as sinks for reactive oxygen species in some non-
1301	crystalline silica polymorphs (Brinker et al., 2020; Croissant et al., 2020).
1302	
1303	SUPPLEMENTARY INFORMATION
1304	Supplementary File 1: Summary of the range of crystalline silica contents of natural rocks
1305	and synthetic stone, as well as natural respirable dust ('loess') as determined in this study
1306	(spreadsheet).
1307	
1308	Supplementary File 2: Database of commercial "granite-group" products (spreadsheet).
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1310	Supplementary File 3: Methodology used to calculate the range of crystalline silica contents
1311	in natural rocks and synthetic stone (text and accompanying figure).
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1313	Supplementary File 4: Results of calculating the range of crystalline silica contents in natural
1314	igneous and metamorphic rocks using the calculations specified in Supplementary File 1
1315	(spreadsheet).
1316	
1317	Supplementary File 5: Calculations and data sources that were used to construct Figure 5
1318	(spreadsheet).
1319	
1320	