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# Geologically Inspired Monoliths for Sustainable Release of Essential **Minerals into Drinking Water**

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Supporting Information

**ABSTRACT:** Decreasing mineral content in drinking water is a serious concern especially due to the proliferation of desalination technologies. We present an approach to remineralize water with essential minerals such that their concentrations are at the recommended daily dose. We accomplished this using composite materials whose composition and surface area were tuned to achieve constant release of minerals into water over a prolonged period of time. We developed a nature-mimicking tectosilicate porous composite matrix and used it as a structural framework to incorporate



leachable minerals to the extent of 40% of the whole mass, which were released into the water during its functional working life. Release of not only the common macro minerals but also the vital trace minerals was possible in this work. Compacted composites of this kind have been used to create mineralization cartridges. The greenness of these composites evaluated from several sustainability metrics shows that the manufacturing process has minimum or negligible carbon emission, E-factor, and energy consumption. This methodology may be extended to encompass all the essential minerals expected to be present in water.

KEYWORDS: Essential minerals, Remineralization, Drinking water purification, Reverse osmosis, Tectosilicate monoliths

# INTRODUCTION

Minerals play a pivotal role in the smooth functioning of metabolism in life forms including humans and thus directly or indirectly affect their well-being. Human nutritional requirements demand at least 23 mineral elements which are spread across nutrient classes like macronutrients and micronutrients. The macronutrients are carbohydrates, fats, fibers, proteins, and water. Almost 99% of the mass of the human body is made up of elements of macronutrients, namely, oxygen, carbon, hydrogen, and nitrogen. The micronutrients are vitamins and minerals, and the latter are the chemical elements required by life forms.<sup>1</sup> They are further classified into macro and trace minerals. Macro minerals, namely, potassium, chloride, sodium, calcium, magnesium, and phosphorus, the abundant constituents of tissues, are involved in central functions such as the maintenance of osmotic pressure and membrane potential. They play dynamic roles in electrolytic balance, acid-base balance, protein synthesis, control of cellular growth/differentiation, immune system function, composition of bones and teeth, etc.<sup>2</sup> The other elements present in the human body are referred to as the trace or oligo elements, namely, iron, zinc, fluoride, manganese, boron, copper, iodine, selenium, molybdenum, vanadium, chromium, tin, and cobalt, which

are crucial and promote a healthy life style.<sup>3</sup> Trace minerals in general play an important role as cellular antioxidants, and each of them possess special contributions of their own. Selenium regulates thyroid hormone action and the oxidation/reduction status of vitamin C and other molecules. Metabolic function of copper includes collagen and elastin synthesis and formation of hemoglobin, red cells, and enzymes. Manganese is involved in the formation of bone. Of the trace elements, molybdenum acts as a cofactor for enzymes involved in catabolism of sulfur containing amino acids, purines, and pyrimidines. Cobalt is a part of the vitamin cyanocobalamin. Vanadium contributes to the regulation of Na<sup>+</sup>/K<sup>+</sup>-ATPase, phosphoryl transfer enzymes, adenylate cyclase, and protein kinases.<sup>4</sup>

A deficiency in the above-mentioned dietary minerals by definition must adversely affect the optimal biological function, and this change should be preventable or reversible by providing physiological amounts of the specific mineral. For example, magnesium (Mg<sup>2+</sup>) is an element of critical nutritional importance and is a cofactor in over 600 enzymatic

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reactions vital for metabolic pathways like DNA/RNA/ protein/ATP synthesis, cellular energy production, energy storage, glycolysis, and cellular secondary messenger systems.  $Mg^{2+}$  regulates the cellular ion channels, transporters, and signaling, which govern calcium, potassium, and sodium movement in and out of the cell. Therefore, deficiency of magnesium alone can lead to a cascade of malfunctions in the human metabolism.<sup>5</sup>

The chief source of mineral intake for human beings is through food and water. Essential inorganic minerals like calcium, magnesium, sodium, potassium, iron, and zinc which occur at milligram per kilogram (mg/kg) quantities in the body are crucial for the human system.<sup>6</sup> But the enteral suction of them is influenced by the source of intake as well. Since cooking processes can produce chemical transformations, they change the major nutrient composition and consequently affect the metal bioaccessibility and bioavailability.<sup>4</sup> Food processing and preservation techniques like freezing, canning, refining, and dehydrating contribute to the loss of various essential and trace minerals.<sup>7</sup> Usage of herbicides like glyphosates have been reported to reduce the physiological levels of essential mineral uptake by plants.<sup>8</sup> So, the mineral intake through the fluid pathway plays a key role in maintaining their balance within the body. Physiologically, waterborne minerals are in ionic form which tend to be bioavailable and are easily absorbed by the human gastrointestinal tract.<sup>9</sup> Although most of the surface waters and ground waters contain varying concentrations of minerals ( $\geq$ 250 ppm), the hardness is removed which removes the essential minerals too. As divided doses throughout the day can promote mineral absorption efficiently in comparison to bolus consumption, it can be said that the best source to compensate these deficiencies is through mineral enriched waters.<sup>10</sup>

With shrinking freshwater reserves and rising water demands, water-stressed countries have begun to augment available water resources by utilizing oceans and inland seas as alternative water sources.<sup>11</sup> In a typical desalination unit, pressurized input water with high TDS (total dissolved solids) is fed to a membrane module, where a pure water permeate and a concentrate containing the retained salts are produced. This pure water is blended with 20% of the source water, a process called split treatment. In most cases, lime softening or ion exchange is performed to balance the demineralized water.<sup>12,13</sup> Nevertheless, both these approaches do not solve the problem completely, namely, the loss of essential and trace minerals. Numerous facilities have been developed without compliance with uniform guidelines, and they lack regulatory monitoring of essential mineral content. Most of the local bottled waters are low in all minerals<sup>14</sup> as they are usually obtained by membrane treatment, reverse osmosis, deionization, or distillation without any post-treatment.<sup>15</sup> Loss of essential minerals due to desalination especially by reverse osmosis has been a concern in the recent past.<sup>16</sup> A larger loss of magnesium has been detected in Israel in the recent studies as a result of desalination.<sup>17</sup> Based on existing knowledge and the fact that desalinated technologies constitute an increasing market in the world and may affect health, we can see an urgent need for more appropriate solutions for their mineral enhancement.

Controlled release of ions into water represent a promising technology for enriching the mineral content of potable water. As mentioned above, drinking water needs to have a certain minimum amount of macro- and trace minerals for it to provide health benefits.<sup>2,7</sup> Geological studies on some prominent water basins across the world have shown the presence of various essential minerals. This is attributed to the silicate weathering that happened over a period of time.<sup>18,19</sup> Dissolution of sparingly soluble salts has been of partial interest in the context of pH control and water stabilization,<sup>20</sup> but these reports are not concerned with the release of essential and trace mineral ions for enriching the water quality. In order to mimic the geological conditions, we attempted to create stable structures of three-dimensional framework silicates called tectosilicates by embedding the desired mineral of interest in a leachable form. If each tetrahedron in the framework contains silicon as its central atom, the overall structure becomes electrically neutral (as in quartz). Whereas in tectosilicate structures, some of the tetravalent silicon are replaced by trivalent aluminum, giving rise to a deficiency of positive charge. The so-developed charge is balanced by the presence of cations elsewhere in the structure,<sup>21</sup> thereby trapping minerals within the porous three-dimensional framework cages. Many of the counter-cations in the network (i.e., exchangeable cations) are weakly held and thus are free to exchange with others in solution.<sup>22</sup> Since the Si–O are strong covalent bonds and the structure is interlocking, the tectosilicate minerals tend to have high hardness.

In our past work, we had shown sustainable release of carbonates into water from a composite matrix composed of porous inorganic networks.<sup>23</sup> In this work, we extend the science of constant release from such stable composites to a range of materials so that ionic release is controlled to the required level. A stable and robust composite of silica was achieved at a temperature below the melting point of the chosen mineral using carbonates as fluxes and by optimizing several combinations of the raw materials. The prepared monolith works as a controlled mineral releasing system maintaining an equilibrium concentration above which further release does not occur. The pores are small enough allowing the minerals to be preserved within, yet allowing sufficient interaction with water. By tuning the composition as well as the particle size, we demonstrate constant release of ten different ions such that their concentrations in water match with the recommended daily allowance (RDA) or dietary reference intake (DRI).<sup>24</sup> These ten minerals chosen for targeted release into water are categorized as four major and six trace minerals based on their quantity of recommended intake per day. The four major minerals shown here are magnesium, sodium, potassium, and zinc with RDAs of 320, 1500, 4700, and 8 mg/day, respectively. The six trace minerals shown here include manganese, copper, selenium, molybdenum, vanadium, and cobalt and with RDAs of 1800, 900, 55, 45, 25, and 0.06  $\mu g/day$ , respectively. Such materials have been compacted to produce mineral release pellets to be put as components of inline filters to create affordable, optimally mineralized water. The concentrations of mineral intake from food and water are classified in Table 1 (see later in the text) with reference to the National Diet and Nutrition Survey (NDNS) and World health organization (WHO) report on trace minerals. We propose that all the essential minerals in water could be provided with such a strategy, yet delivering 100% safe potable water solving one of the important problems of the current water purification strategy.

These nature-inspired monoliths prepared in this work are in consonance with sustainability and greenness. A sustainable development is defined as the advancement that meets the

Table 1. Daily Recommended Intake of Essential Minerals for Human Metabolism (macro and trace), Recommended by NDNS and WHO, Their Tolerable Limit (left),<sup>4,9,24</sup> and Mineral Concentrations Supplemented through Designed Monoliths Given as ppb/cm<sup>2</sup> (right)

s.n	Туре	Element	RDI (mg/day)	Tolerable limit (mg/day)	Total intake (food**) (mg/day)	Total intake (water***) (mg/day)	Reference for intake values	Cobalt	0.002		
1	Macro	Calcium	1000	4500	830	600	1990 NDNS	Vanadium	0.18		
2	Macro	Magnesium	320/420*	1400	280	100	NDNS 1986/7				
3	Macro	Zinc	08/11*	40	9.8	10	1986/87 NDNS				
4	Macro	Potassium	4700	4900	2800	24	NDNS, 1986/7	Manganese	0.09		
5	Macro	Sodium	1500	2300	7200	20-250	1986/1987 NDNS				
6	Trace	Selenium	0.055	0.4	0.039	NA	1994 TDS				
7	Trace	Chromium	.025/.035*	0.05	0.1	0.002	1997 TDS	Molybdenum	0.12		
8	Trace	Copper	0.9	10	1.4	.6	1986/87 NDNS		· · · · · · · · · · · · · · · · · · ·		
9	Trace	Manganese	1.8/2.3*	11	4.9	0.1	TDS, 1994				
10	Trace	Molybdenum	0.045	2	0.11	0.02	1994 TDS	Selenium	2.3		
11	Trace	Cobalt	0.00006	1	0.012	0.02	1994 TDS				
12	Trace	Vanadium	0.025	10	0.013	0.01	1980 UK TDS				
13	Macro	Phosphorus	700	4000	1260	4.4	NDNS 1986/7	Copper	0.8		
14	Macro	Chloride	2300	3600			-				
15	Trace	Fluoride	3/4*	10	NA	NA	-				
16	Trace	Iodine	0.15	1.1	0.22		1986/87 NDNS	Zinc		167	
17	Trace	Sulphur	NA		NA	NA	-				
18	Trace	Boron	1	13	1.5	0.2-0.6	1994 TDS				
19	Trace	Iron	18/8*	45	12	0.4	1986/87 NDNS	Magnesium		183	
20	Trace	Nickel	NA	1	0.13	0.04	1997 TDS		A 444481 A 444681		
21	Trace	Tin	0.01	2	1.8	NA	TDS, 1994				
22	Trace	Silicon	NA	560	50	10	Bowen and Peggs 1984	Sodium		76	
23	Trace	Aluminium	NA	0.2	14	.2 to 2	WHO trace				
24	Trace	Germanium	NA	0.007	0.004	NA	1994 TDS	Potassium		160	
25	Essential	Oxygen	No limits	No limits	No limits	NA	nil	1 otassium		100	
26	Essential	Hydrogen	No limits	No limits	No limits	NA	nil				
27	Essential	Nitrogen	No limits	No limits	No limits	NA	nil	0	.001 0.1 10	1000	
28	Essential	Carbon	No limits	No limits	No limits	NA	nil			1000	
* - Recommended intake for Female/Male *** - Assuming drinking water intake of 2 L/day ** - Mean value NA - No data available								Average release (ppb/cm <sup>2</sup> /10 min)			

needs of the present without depletion of natural resources for the future generations to meet their own needs. Sustainability metrics and indices are measures of sustainability, which allows a clear assessment of a product and its manufacturing process. The essence of greenness can be defined as the efficient utilization of raw materials and elimination of waste in the production and application of a material. This also includes the efficiency in energy consumption, preferably the renewable resources. The use of toxic and/or hazardous solvents and reagents in the manufacture and application of a material should be minimized as much as possible.

# EXPERIMENTAL SECTION

Natural minerals of the tectosilicate group have three-dimensional arrays of interconnected silica and alumina tetrahedra linked to each other through shared oxygen atoms. If all of the corner oxygens are shared with another  $SiO_4$  tetrahedra, then a framework structure develops. As a result, a crystal structure consisting of interconnected cavities and channels are formed. Our objective was to create such a nature-mimicking template of tectosilicate loaded with minerals of interest, held strongly along with controlled release. The mineral releasing monolith was synthesized using a solid state route. It was made by melting silica and alumina at the lowest possible temperature such that the incorporated mineral ions do not decompose. Various optimization studies were undertaken with respect to the Si–Al ratio, which ensures that the stability of the scaffold is maintained while the chosen cations are incorporated into its structure.

All the chemicals used were purchased from Sigma-Aldrich and used as such. Unless otherwise specified, all the chemicals used were of analytical grade.

Synthesis of Sustained Mineral Releasing Materials. Due to the requirement of the three-dimensional network that has chemical inertness and structural integrity, silica and alumina were our choices in mimicking mineral resources present in nature. The metal salt containing silica monoliths were, in general, comprised of a porous Si-O-Al scaffold loaded with the source of the chosen mineral, namely, magnesium carbonate (MgCO<sub>3</sub>), sodium carbonate  $(Na_2CO_3)$ , potassium carbonate  $(K_2CO_3)$ , copper carbonate (CuCO<sub>3</sub>), zinc oxide (ZnO), selenium trioxide (SeO<sub>3</sub>), cobalt oxide (CoO), manganese dioxide (MnO), vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>), or molybdenum(VI) oxide (MoO<sub>3</sub>). The preference of carbonate or oxide forms of the mineral source was made based on the need for providing controlled bioavailability. For example, molybdenum(VI) oxide and calcium molybdate are absorbed well from the gastrointestinal tract. Zinc is an exception where zinc oxide and zinc carbonate possess a similar bioavailability. The minerals recommended in trace concentrations were chosen as oxide forms with  $\sim$ 20% bioavailability, whereas the macro minerals were in the carbonate forms with  $\sim 80\%$  bioavailability. Figure 1 describes a schematic outline of the synthesis of the designed monolith and a water purification method based on the same.

Compositions of the raw materials were optimized in such a fashion that they form tectosilicate frameworks mimicking those present in nature. The framework structure and properties of the scaffold can be correlated with the molar ratio of Si/Al and was thus maintained in the window of 10–20. This provided us with the required properties of sustainable release, formation temperature < 850  $^{\circ}$ C, and robustness of the product. The composite consisted of 10 wt % of



Figure 1. Schematic representation of the synthesis of mineral ion releasing monoliths (steps 1-4) and a water purification system based on the same. The monoliths are stable solids (in the shape of the mold) which may be combined as a contraption as per the need.

 $Na_2CO_3$  which served as a flux to maintain the formation temperature as well as a source of sodium. The targeted mineral ions of interest were taken at a concentration of 15–25 wt % each, as per the recommended release in water. Four such monoliths,  $M1_{(Na-Zn-Se)}, M2_{(Na-Cu-Zn)}, M3_{(K-Co-Mo-V)}$ , and  $M4_{(K-Mg-Mn)}$  with 2–4 targeted minerals in each were synthesized in this work, thus demonstrating the release of a total of ten different mineral elements in water. Images of these ion-containing monoliths are presented in Figure 1.

The mixture of raw materials were homogenized and packed in molds and sintered at 750–850  $^{\circ}$ C for 1 h. The metal loading was performed homogeneously such that there were no specific regions of aggregation. This was important in achieving constant release of mineral ions in water. Decomposition temperatures of most of the chosen minerals were above 850  $^{\circ}$ C at atmospheric pressure.<sup>25</sup> The sintered monolith was cooled to room temperature followed by washing with water at ambient conditions up to 12 h and was used as such for further experiments. A contraption of such monoliths was made such that they can be used in an in-line water purification system.

Characterization Techniques. Metal-loaded monoliths were dried for 24 h at 60 °C in air and examined in detail for their morphological characteristics and elemental composition and were mapped for the elemental distribution using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) equipped with energy dispersive spectroscopy (EDS). HRTEM images of the sample were obtained with JEM 3010 (JEOL, Japan) microscope operating at 300 kV with an ultrahigh resolution polepiece. Elemental mapping using TEM was done on an Oxford Semistem EDS system. The samples for HRTEM were prepared by dropping the dispersion on amorphous carbon films supported on a copper grid and subsequent drying. FEI Quanta 200/EDS was used for SEM. Identification of the tectosilicate and mineral phase(s) of all the samples was carried out by X-ray diffraction (XRD) using Cu K $\alpha$ radiation at  $\lambda = 1.5418$  Å (Bruker AXS, D8 Discover, U.S.A.). Fourier transform infrared (FTIR) spectra of the samples were collected using a PerkinElmer FTIR spectrometer. The spectra were collected in the range of 450-4000 cm<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCA Probe TPD of Omicron Nanotechnology with polychromatic Mg K $\alpha$  as the X-ray source (hv = 1253.6 eV), and the binding energy was calibrated with respect to C 1s at 284.5 eV. The concentrations of mineral ions released in water were measured using inductively coupled plasma mass spectrometry (ICPMS) (PerkinElmer NexION 300X ICPMS).

**Kinetics of Ion Release.** Sustained release of minerals from the synthesized monoliths and their kinetics of release were studied using the following experimental procedure. About 500 mg of the as

prepared monolith pellets were rinsed thoroughly with distilled water before the experiments. Later, they were shaken briefly in 500 mL of deionized water. Concentrations of minerals released in the test water at different contact times (with 10 min interval) were measured based on the measurements at each step using ICPMS. The instrument was calibrated using commercial standards of selected ions. The measurements were performed using deionized water, and the initial concentration of any ion present was monitored for every individual experiment and was considered as blank.

Sustained Release of Minerals in Water. The performance of the material under continuous flow of water was tested in the cartridge mode. A cartridge containing 1 L of deionized water was treated with 1 g of the monolith material. After 15 min of standing time, the concentration of the released mineral was tested in the treated water. The cartridge was drained and filled with a fresh batch of deionized water (1 L), and the above procedure was repeated to monitor the release. This test was repeated up to 50 cycles. After every ten cycles of the above procedure, the material was dried for 18–20 h at room temperature and was tested for further mineral release.

*Prototype.* After evaluating the release performance of the material in batch and cartridge experiments, a mineral releasing prototype was developed. About 10 g of the synthesized composite pellets (each pellet of  $\sim$ 1 g) was packed in a contraption that was assembled in-line along with a deionized water reservoir. The inlet and outlet flow rates of water were controlled such that there was sufficient contact time for the mineral to be released into it. The output water was analyzed after acidification (5% HNO<sub>3</sub>) and digestion, to ensure that all particulate matter that leached out, if at all, was also evaluated.

#### RESULTS AND DISCUSSION

Tectosilicates have been commonly found in nature as well as synthesized artificially. Depending upon the type of raw materials used and the methods of synthesis adopted, properties of these tectosilicates would vary and, hence, their application can be modified. These tectosilicates in nature are often formed as a volcanic glass in various geological environments, under variable geochemical and physical conditions. Keeping this in view, a nature-mimicking scaffold loaded with mineral ions of interest were synthesized, and their properties are presented in the following.

**Characterization of Sustained Mineral Releasing Monoliths.** The SEM and TEM images of the granular particles of the monolith and their chemical compositions are



**Figure 2.** (A) SEM image of the material and the corresponding EDS spectra along with the elemental maps (right). ( $B_1$ ) TEM image of a grain of the material and ( $B_2$ ) the corresponding EDS spectra along with the elemental maps of the same grain (right). ( $B_3$ ) Lattice resolved image and its FFT pattern (inset).

shown in Figure 2. A granule of ~500  $\mu$ m of M<sub>1</sub> (see the Experimental Section) confirms the porous but crystalline morphology. Porosity is evident in the SEM image shown in Figure 2A, and the corresponding EDS confirms the presence of silicon, aluminum, sodium, zinc, and selenium. Elemental mapping of the metal ion-containing single grain of the monolith is presented in the inset. We can clearly see that the ions of interest are uniformly dispersed within the silica template and no specific aggregation of metals is found. This provides a uniform dissolution of the minerals when in contact with water. TEM image of a grain of material is shown in Figure 2B<sub>1</sub>. No metal particles can be detected, which means that the metal ions are located regularly along or in the pore walls of the silica network. The corresponding EDS spectra along with the elemental maps are shown. Also the lattice resolved image in Figure 2B<sub>3</sub> shows the lattice planes of crystallites at 0.29 nm indexed to 410 (hkl) corresponding to JCPDS PDF no. 88-2371 and at 0.25 nm indexed to 300 (hkl) corresponding to JCPDS PDF no. 22-0014. The fast Fourier transform (FFT) pattern in the inset of Figure 2B<sub>3</sub> shows crystalline nature of the monolith. SEM and TEM images of the granular particles of the monoliths, M2, M3, and M4, and their chemical compositions are shown in Figures S1-S3, respectively. Thus, SEM, TEM, EDS, and elemental mapping establish the formation of crystalline silicate monoliths with mineral ions evenly distributed in the network.

The X-ray diffraction patterns of the precursor composition and the amended granular composite are shown in Figure 3A,B. The pattern was analyzed using X'pert HighScore Plus Rietveld analysis software loaded with ICDD database, PDF-2 and JCPDS. Initially, the tetragonal phase of SiO<sub>2</sub> (00-001-0438) and Al<sub>2</sub>O<sub>3</sub> [00-037-1462] and monoclinic phases of SeO<sub>2</sub> [00-004-0429], ZnO [01-079-0207], and Na<sub>2</sub>CO<sub>3</sub> [01-071-1833] were the principal components of the precursor of composite M1 (Figure 3A). Upon heating, the pattern shows peaks at 2 $\theta$  (degree) at 22.00, 28.47, 31.49, 36.13, 36.41, 47.10, and 48.65 which correspond to (101), (111), (102), (200), (112), (113), and (212) planes of cristobalite (39-1425), a framework silicate mineral having a tetragonal crystal structure along with Al<sub>2</sub>O<sub>3</sub> (hexagonal) and Na<sub>2</sub>O (cubic) (Figure 3B). Cristobalite present in nature is a high temperature SiO<sub>2</sub> polymorph and occurs in thermally metamorphosed sandstones. Despite the dominating cristobalite phase, the matrix also contains Al<sub>2</sub>(SeO<sub>4</sub>)<sub>3</sub> and Zn<sub>6</sub>Al<sub>12</sub>Si<sub>12</sub>O<sub>48</sub> which are embedded within the tectosilicate network. It should be noted that the decomposition temperatures of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> are 858 and 898 °C, respectively, at atmospheric pressure.<sup>25</sup>

Similarly, the XRD pattern of M2 was matched with gehlenite and leucite (Figure S1A), M3 was matched with cristobalite and feldspar (Figure S2A), and M4 was matched with sanidine and orthoclase (Figure S3A).<sup>26</sup> These tectosilicates are composed of silica and alumina tetrahedra linked to each other through shared oxygen atoms. Because of the extended isomorphic substitution of Si<sup>4+</sup> by Al<sup>3+</sup> in the tetrahedra, a large unsatisfied negative charge is produced in the lattice. This negative charge is balanced by cations, which are retained by electrostatic bonds and move onto the surface or into the crystal structure of the tectosilicate network. The FTIR spectra in Figure 3C and Figures S1C, S2C, and S3C show metal-coordinated unidentate, bidentate, and bridged carbonate species along with Si-O-Si bending and Si-O stretching frequencies.<sup>27</sup> Figure 3D depicts the XPS analysis of the material. Deconvoluted spectra shown in Figure 3D (i) confirm the presence of oxygen, where O 1s peaks appear in the range of 531.5-532.0 eV for metal carbonates and 532.0-533.0 eV for SiO<sub>2</sub>. The C 1s appears at 284.8 eV due to C-C and at 288.5 eV due to O-C=O. Se 3d and Zn 2p are shown in Figure 3D (ii-iv). Two peaks located at 1043.1 and 1020.0 eV correspond to Zn  $2p_{1/2}$  and Zn  $2p_{3/2}$ , respectively, due to Zn<sup>2+</sup>, and the 3d peaks of selenium split into two well-defined peaks as  $3d_{3/2}$  and  $3d_{5/2}$ , which appeared at binding energies of 56.5 and 55.7 eV.<sup>28,29</sup> These indicate that the chosen mineral ions of interest are embedded in the  $SiO_2$  matrix.

**Kinetics of Mineral Release from the Material.** From the release data presented in Figures 4 and 5, we understand that the targeted mineral ions are continuously leached into the water retaining the framework which is represented by negligible loss of the weight of the pellet (Figure S4A). Since the loss of weight is negligible after each release, all the mineral release experiments were done considering the same surface area calculated in the beginning. As the Al<sup>3+</sup> gets into the crystal lattice of the tectosilicate, it is not released into the water (Figure S4B). The structural integrity of the monolith is evident from the SEM image, and the corresponding EDS spectra along with the elemental maps and the powder XRD pattern of the material after 120 min of leaching are presented in Figure S5.

The concentration of mineral ions released into the water from the prepared monolith is highly tunable at relevant temperatures (5-35 °C) and varying TDS (100–1000 ppm). The release does not alter the pH of the water beyond the permissible limit of 6.5-8.5.<sup>30</sup> The release occurs within 5–15 min of contact time, and concentration of the release does not exceed their RDAs even when there is a prolonged contact time, tested up to 160 min in batch mode shown in Figure 4 for both major and trace minerals. The concentration of minerals released in deionized water is represented as ppb/cm<sup>2</sup> and reaches equilibrium. Average releases of 183 ppb of Mg<sup>2+</sup>/ cm<sup>2</sup>, 76 ppb of Na<sup>+</sup>/cm<sup>2</sup>, 160 ppb of K<sup>+</sup>/cm<sup>2</sup>, 167 ppb of Zn<sup>2+</sup>/

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**Figure 3.** Powder XRD pattern of the precursor material (A) and the as prepared sintered pellet (B). The sintered pellet is compared with the low temperature form of SiO<sub>2</sub> cristobalite (JCPDS 39-1425). Specific features matching  $Al_2(SeO_4)_3$  (JCPDS 22-0014) and  $Zn_6Al_{12}Si_{12}O_{48}$  (JCPDS 88-2371) are also observed. (C) Infrared spectrum of the mineral composite. (D) (i) XPS of the mineral ion releasing monolith. (ii–iv) Deconvoluted XPS spectra of corresponding Se 3d, C 1s, and Zn 2p regions, respectively.

cm<sup>2</sup>, 5 ppb of Se<sup>6+</sup>/cm<sup>2</sup>, and 0.9 ppb of Cu<sup>2+</sup>/cm<sup>2</sup> were observed. The possible release mechanism of the mineral ions is due to the intricate scaffold architecture of the calcined silica that allows only limited contact of water through its channel to dissolve it.

The performance of the material was studied under cartridge mode with continuous flow of water and sustained release data of mineral ions from the four major silica scaffolds, namely, M1<sub>(Na-Zn-Se)</sub>, M2<sub>(Na-Cu-Zn)</sub>, M3<sub>(K-Co-Mo-V)</sub>, and M4<sub>(K-Mg-Mn)</sub>, are shown in Figure 5. This was tested up to 50 cycles which demonstrates a constant and sustained release of the selected essential and trace minerals in drinking water, namely, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Se<sup>6+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup>, V<sup>5+</sup>, Co<sup>2+</sup>, and Mo<sup>6+</sup>, in a strictly controlled fashion such that their concentrations match the RDA levels. Each data point is an average of triplicate experiments. After every ten cycles of exposure to water, the material was drained and dried for 18-20 h at room temperature and was tested for further release. After every step of drying of the sample, an increased release of sodium, potassium, and magnesium in the first round of exposure was observed (shown as a spike in the graph). The structural cavities and entry channels leading into the scaffold are large enough to retain water molecules within them, resulting in

prolonged soaking of the material by the stagnant water during the slower rate of drying at room temperature.<sup>23</sup> The dissolved cations inside the pore are released faster when the material is soaked in a fresh batch of water. This is not of consequence to the water purification device as the initial water collected is often discarded in typical reuse of the mineralization cartridge.

After evaluating the release performance of the material in batch and cartridge experiments, a mineral releasing prototype was developed as shown in Figure S6A. The efficiency of release from the contraption that was assembled in-line along with the deionized water reservoir is shown in Figure S6B–D. The inlet and outlet flow rates of water were controlled such that there is sufficient contact time for the mineral to be released into it.

Once released into water, understanding the speciation of ions is essential in order to confirm their bioavailability during consumption. Thus, a speciation diagram was prepared by including all the ions released into the system at pH = 7.5 and T = 25 °C. Figure S7 shows the number of complexes formed due to speciation of mineral ions at their specific release concentrations. The speciation diagram was prepared using simulations run on Visual MINTEQ software version 3.1 (freeware, available at http://vminteq.lwr.kth.se).

Research Article



## Time (min)

Figure 4. Kinetics of targeted mineral release from the monolith upon prolonged period of exposure to water. Equilibrium was attained typically beyond 100 min. The units are expressed in  $ppb/cm^2$ , and the error bars are standard deviations from triplicate experiments.



Figure 5. Sustained release of desired ions from the synthesized pellets, for up to 50 cycles. Ten cycles per day were conducted. Units are in  $ppb/cm^2$ . A blank water was tested at the beginning of every 10 cycles designated as 0  $ppb/cm^2$  concentration. Error bars are standard deviations from triplicate experiments.

Sustainability Metrics Parameters											
materials	mass intensity (kg/kg)	solvent intensity (kg/kg)	reaction mass efficiency (%)	energy consumption (kWh)	E-factor (kg/kg)	CO <sub>2</sub> emission (mg/kg)					
$M1_{\left(Na-Zn-Se\right)}$	1.204	4.75	83	3.2	0.025	40					
$M2_{(Na-Cu-Zn)}$	1.388	5.47	72	4.0	0.060	80					
$M3_{(K-Co-Mo-V)}$	1.408	5.55	71	3.2	0.046	80					
$M4_{(K-Mg-Mn)}$	1.428	5.63	70	4.0	0.040	70					

Therefore, by designing a mineral ion loaded silica monolith of tectosilicate structure, release of essential major minerals and trace minerals was achieved for remineralization of drinking water. An average concentration of the selected ten minerals released by the designed monolith is shown in Table 1. The table highlights the essential elements for human metabolism (macro and trace) recommended by National Diet and Nutrition Survey (NDNS)<sup>24</sup> and World health organization (WHO) report on trace elements,<sup>4</sup> their tolerable upper limit, total intake from food and water, and mineral concentrations supplemented via the designed monoliths.

**Sustainability Metrics Evaluation.** The "greenness" of all the four materials and their synthesis procedures were determined in terms of relevant sustainability parameters, as shown in Table 2.

*Raw Materials.* The major raw materials used for the scaffolds were silica/alumina which are sustainable in nature as they are known to be nonecotoxic and nonhazardous.<sup>31</sup> Crystalline silica (quartz) is not known to be ecotoxic; i.e., there are no data that suggest that crystalline silica (quartz) is toxic to birds, fish, invertebrates, microorganisms, or plants. The mass-based sustainability metrics were assessed where the mass intensities for  $M1_{(Na-Zn-Se)}$ ,  $M2_{(Na-Cu-Zn)}$ ,  $M3_{(K-Co-Mo-V)}$ , and  $M4_{(K-Mg-Mn)}$  were close to 1, indicating maximum conversion of raw materials into useful products with very high reaction mass efficiencies. As far as usage of solvents is concerned, the solid state synthesis route involves solvents in meager amounts, thus giving negligible water intensity numbers.

*Energy Consumption.* For getting the desired framework of Si/Al, the monolith materials had to be sintered at high temperatures in the furnace, which mainly contributes to the electrical energy consumption. A maximum energy usage of 4 kWh per kg of material was observed in this case which includes homogenization, compaction, and sintering. However, release of minerals from the composite occurs by diffusion/ dissolution, and no energy is consumed during the process of mineralization of water. The energy used for production is comparatively less significant than the reported energy consumption required for the operation of reverse osmosis for per cubic meter of purified water<sup>32</sup> (2.2–6.7 kWh/m<sup>3</sup>). The cumulative energies consumed for the production of polymers<sup>33,34</sup> vary between 23–40 kWh/L.

Resulting Emissions. The synthesis, washing, and application of these monoliths generate a minimal amount of waste which can be seen by the calculated E-factors, one of the most important parameters used to evaluate sustainability. Finally, as a result of sintering of carbonate salts at high temperatures, there is evolution of some amount of carbon dioxide, shown as  $CO_2$  emission values (<80 mg/kg). However, we can work toward minimizing the gas evolution by further optimizing the sintering temperature by addition of green fluxes. Though the total carbon footprint of a product is made up of emissions produced at every stage of the life cycle, this value depicts only the gate-to-gate approach and focuses on only the synthesis procedure and ignores all steps before and after. A cradle-togate assessment of the material's  $CO_2$  emission including the manufacture of raw materials and production of the designed monolith is presented in Table S1. The  $CO_2$  emission due to the transport and disposal of finished goods is not included, and therefore it is not a cradle-to-grave assessment.

Toxicity potential. Ions like  $Se^{6+}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$ ,  $V^{5+}$ ,  $Co^{2+}$ , and  $Mo^{6+}$  are trace minerals in the human body. Therefore, they are required in meager amounts, and concentrations beyond a particular limit show acute oral toxicity. Therefore, the manufacturing process should undertake precautionary measures. The LD 50 values of all the raw materials used for the composite preparation are shown in Table S2.

Disposal of Waste. Once the material is exhausted after complete leaching of minerals, the expected leftover material is the silica scaffold, which is again environment friendly. So, the issue of waste disposal is inherently solved in this case.

The equations used to for the evaluations of the sustainability metrics are listed in the Supporting Information (eqs 1-5).

## CONCLUSION

We report a composite material, forming a structurally stable monolith, releasing selective essential mineral ions in water at a fixed concentration for a prolonged period to enhance the quality of drinking water. Characterization studies indicate that the synthesized materials match tectosilicates present in nature. We have achieved the formation of robust three-dimensional tectosilicate matrices at temperatures below their standard formation temperatures, which entrap the cations of interest. The monoliths have been prepared with inert templateforming materials mimicking nature, which releases mineral ions at precise concentrations for each mineral, as described earlier. The matrices do not change even upon longer periods of exposure to water at room temperature. Such concentrations of minerals can reduce the occurrences of conditions such as osteoporosis, ulceration of epithelial lines, and other mineral deficiencies, observed in several parts of the world due to the consumption of demineralized water. This material can be used along with several water purification technologies to develop a synergetic enhancement system, delivering mineral-balanced potable water.

Although research shows that other trace elements like nickel, chromium, etc. are reported to be essential in human metabolism, there is no clear evidence on the RDA for these minerals. If known, several of these ions can also be released controllably in a similar fashion so that "enhanced" water may be supplied. By modifying the surface charge and surface properties using organic molecules or surfactants, a similar monolith with anion releasing property can be designed. Such modifications of the designed monolith with different

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b01902.

Scanning and transmission electron microscopic images, energy dispersive X-ray spectra with elemental mapping from both SEM and TEM, XRD and XPS of the composites  $M2_{(Na-Cu-Zn)},\ M3_{(K-Co-Mo-V)},\ and M4_{(K-Mg-Mn)}$ , and schematic of a prototype setup and kinetics of release of ten minerals during exposure to continuous flow of water and their speciation data (PDF)

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T.P. and S.J.R. designed the experiments. S.J.R., A.M., P.S., A.A.K., Md.R.I., and S.M. performed the experiments. T.P., L.P., and J.R.S. analyzed the data and wrote the paper, with input from all authors.

#### Notes

The authors declare no competing financial interest.

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