Silicates, Aluminosilicates and Biogenic Silica

Catherine E. Housecroft

*Correspondence: Prof. C. E. Housecroft, E-mail: catherine.housecroft@unibas.ch

Department of Chemistry, University of Basel, BPR 1096, Mattenstrasse 24a, CH-4058 Basel

Abstract: Silicate and aluminosilicate minerals are hugely important in the Earth’s crust; this article introduces three mineral classes and describes the origins of biogenic silica.

Keywords: Aluminosilicate · Biogenic silica · Education · Silicate · Structure–property relationships

In an earlier Education Column,[1] we described the assembly of the 3D-structures of ice and SiO₄ using tetrahedral building blocks. We now extend this concept to silicate minerals and biogenic silica. Of the 118 chemical elements, only a few are abundant on Earth. 46.6% of the Earth’s crust consists of oxygen, primarily in the form of oxides, carbonates, sulfates, silicates and aluminosilicates, while 27.7% comprises silicon compounds, mainly in the form of sand and quartz (SiO₂). Silicates and aluminosilicates. Aluminium occurs in the Earth’s crust to an extent of 8.1%, largely as bauxite (a mixture of Al₂O₃ and Al(OH)) and aluminosilicates.

Silicate minerals are divided into six classes according to their building blocks, and we consider three of these. The mineral olivine is an example of a nesosilicate and contains discrete [SiO₄]⁴⁻ units. The chemical formula of olivine is (Mg,Fe)₂SiO₄. The (Mg,Fe)²⁺ formulation signifies that the mineral can contain Mg²⁺, Fe²⁺, or a mixture of Mg²⁺ and Fe²⁺ ions. Figs 1a and 1b show the arrangement of four adjacent [SiO₄]⁴⁻ ions in crystalline olivine. The Mg²⁺ and/or Fe²⁺ ions are located between the [SiO₄]⁴⁻ tetrahedra with electrostatic interactions between the cations and anions. Fig. 1c shows one unit cell in crystalline olivine with the metal ions highlighted in orange. Mg-rich olivines have a green or yellow appearance (Fig. 1d) while Fe-rich olivines are brown or black. The pale green mineral peridot is gem-quality Mg-rich olivine.

In the [SiO₄]⁴⁻ units in olivine, each O atom is terminal and carries a 1⁻ charge. Figs 2 and 3 demonstrate that if two or three O atoms per Si form bridges between pairs of Si atoms, the resultant building blocks are single [SiO₄]²⁻/Mg²⁺ (orange) and [SiO₄]⁴⁻ ions. Data: ICSD code 4353.[2] (d) A piece of magnesium-rich olivine (by Rob Lavinsky, iRocks.com – CC-BY-SA-3.0, CC BY-SA 3.0 Commons).<https://creativecommons.org/licenses/by-sa/3.0>, via Wikimedia Commons).

Fig. 1. Olivine, (Fe,Mg)₂SiO₄ contains discrete [SiO₄]⁴⁻ units shown in stick representation in (a), and in polyhedral representation in (b). (c) A unit cell of olivine showing Fe²⁺/Mg²⁺ (orange) and [SiO₄]⁴⁻ ions. Data: ICSD code 4353.[2] (d) A piece of magnesium-rich olivine (by Rob Lavinsky, iRocks.com – CC-BY-SA-3.0, CC BY-SA 3.0 Commons).<https://creativecommons.org/licenses/by-sa/3.0>, via Wikimedia Commons).

Fig. 2. Part of an [SiO₄]²⁻/Mg²⁺ chain present in diopside: (a) stick and (b) polyhedral representations. Data: ICSD code 9672 [2]. (c) Crystalline diopside (Rob Lavinsky, iRocks.com – CC-BY-SA-3.0, CC BY-SA 3.0 Commons).<https://creativecommons.org/licenses/by-sa/3.0>, via Wikimedia Commons).

Silicate minerals containing [SiO₄]²⁻ or [SiO₄]⁴⁻ chains are inosilicates and include the pyroxenes and amphiboles. The prefix ino comes from the ancient Greek ἰνο meaning fibre-like. Typical pyroxenes are silicates of Fe²⁺, Mg²⁺ and/or Ca²⁺, for example diopside, CaMgSi₂O₆ (Fig. 2) and hypersthene, (Fe,Mg)SiO₄. Double-chains are characteristic of the amphibole minerals and an example is tremolite, Ca₂Mg₃Si₄O₁₁(OH)₂. Tremolite tends to exhibit long or column-like crystals (Fig. 3) or may have a fibrous habit. In this latter form, it is found as a component of asbestos which is a mixture of fibrous minerals and is well known for its health hazards.
Fig. 4. (a) Part of a 2D-sheet present in phyllosilicates viewed from above and from the side. (b) Representation of the layer structure of muscovite mica. Data: ICSD code 74608 [2]. The sheets are in polyhedral representation, Al³⁺ ions in pink, and K⁺ ions in purple; OH⁻ ions are omitted. (c) Pieces of muscovite mica; micas cleave easily into very thin sheets. Credit: E. C. Constable 2020.

Increasing the number of Si–O–Si bridge units takes us from 1D-chains to 2D-sheets, and the sheet structure shown in Fig. 4a has the formula [Si₄O₁₀]₄⁻. An example is the mineral talc, Mg₅Si₄O_{10}(OH)₂, which is soft and cleaves into thin plates. This is a lamellar habit. Notice in Fig. 4a that the SiO₄ units within a single sheet all point in one direction giving one ‘flat’ surface. Talc is a member of the chlorite group of minerals, and chlorites and micas belong to the class of phyllosilicates. The prefix phyllo comes from the ancient Greek φυλλον meaning leaf, and describes the ease with which phyllosilicates cleave into thin sheets. In micas, some Si atoms are replaced by Al atoms, thereby making a transition from a silicate to an aluminosilicate. Al and Si are adjacent to one another in the periodic table, and Al³⁺ is isoelectronic with Si. Starting with [Si₄O₁₀]₄⁻, replacement of one Si by Al leads to [AlSi₄O₁₀]₄⁻ which is found in muscovite mica, KAl₃(AlSi₄O₁₀)(OH)₂. There is no structural change on going from the [Si₄O₁₀]₄⁻ sheet in talc to the [AlSi₄O₁₀]₄⁻ sheet in muscovite mica and so both can be represented by Fig. 4a, remembering that in the mica, one in four Si atoms is replaced by Al. In muscovite mica, charge neutrality is attained by a combination of [AlSi₄O₁₀]₄⁻ and OH⁻ with K⁺ and Al³⁺ ions. Muscovite mica possesses the layered structure shown in Fig. 4b. Layers of K⁺ or Al³⁺ ions separate adjacent aluminosilicate sheets, and OH⁻ ions are located in the Al³⁺-containing layers. The material cleaves along the K⁺-containing planes (Fig. 4b) and Fig. 4c shows just how flaky micas are. Micas provide an excellent example of a structure–property relationship.

Weathering of silicate minerals in reactions with environmental CO₂, H₂O and H⁺ releases silicic acid, H₂SiO₄. Condensation of the H₂SiO₄ molecules occurs with elimination of H₂O leading to Si–O–Si bond formation (Eqn. 1) and ultimately to the assembly of amorphous silica [SiO₂·n(OH)₄·]₄⁻, also called opaline silica. Some marine organisms including unicellular algae possess exoskeletons comprised of biogenic silica and these intricate assemblies are constructed from H₂SiO₄ in sea water in a matter of days. When organisms with silica exoskeletons die, the Si–O–Si bond formation is very slowly reversed, regenerating H₂SiO₄.

Some plants deposit biogenic silica in significant amounts and one characteristic example is the common horsetail (Equisetum arvense). The stems and branches (Fig. 5) are stiff and abrasive because of the presence of silica. The plants take up H₂SiO₄ through the roots when the pH is below 9,[3] and accumulate biogenic silica through the condensation reactions described above.

Careful treatment of the plant tissue with acid allows a fragile siliceous framework to be isolated.

In summary, this article has illustrated some of the classes of silicate and aluminosilicate minerals and has shown how the structural features affect the habit (e.g. fibrous, lamellar) of the mineral. Slow weathering of silicates releases silicic acid, and condensation processes in aqueous media produces biogenic silica.

Received: October 26, 2020

[1] C. E. Housecroft, Chimia 2020, 74, 735.
[2] Inorganic Crystal Structure Database (ICSD); https://icsd.products.fiz-karlsruhe.de
[3] P. Labun, D. Grulova, I. Salamon, F. Šeršen, Food Nutr. Sci. 2013, 4, 510.

This column is one of a series designed to attract teachers to topics that link chemistry to Nature and stimulate students by seeing real-life applications of the subject.