



## ZEOLITES: NATURE'S GIFT FOR AGRICULTURE PRODUCTION

<sup>1</sup>\*PRIYA P GURAV, <sup>2</sup>P L CHOUDHARI, <sup>1</sup>ABHAY SHIRALE, <sup>1</sup>BHARAT PRAKASH MEENA, <sup>1</sup>K C SHINOBI, <sup>1</sup>DINESH KUMAR YADAV, <sup>1</sup>A K BISWAS

<sup>1</sup>ICAR-Indian Institute of Soil Science, Bhopal, Madhya Pradesh; <sup>2</sup>ICRISAT Development Centre, Asia Program, Hyderabad, Telangana

\*Corresponding author, Email: priyaguravnbs@gmail.com.

**Z**eolites are aluminosilicate minerals discovered and named by A.A.F. Cronstedt, a Swedish mineralogist in 1756. The mineral has got its name from the two Greek words *zein* and *lithos* (means boiling stones), due to the peculiar frothing characteristics when heated with blowpipe. Zeolites have rigid anionic frameworks with well defined channels and cavities. These cavities may contain exchangeable metal cations, or they may host neutral guest molecules that may be removed or replaced. Origin of zeolites can be either natural or synthetic. However, natural zeolites are mostly volcanic origin.

General formula of natural zeolites is  $M2/n:Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ , where M stands for the extra-framework cation (Bogdanov et al., 2009). Mineral structure of zeolites is based on  $AlO_4$  and  $SiO_4$  tetrahedra that can share 1, 2, or 3 oxygen atoms. Hence, there can be a wide variety of possible structures when the network extended in three dimensions. This unique feature of zeolite is the basis of its microporous structure.

Commercial exploitation of zeolites began around 30 years ago. In nature, nearly 50 exotic and diverse zeolites of various hues and shapes have been identified, several of which have economic potential. World production of natural zeolites is more than 4 million tonnes per year. In India, Maharashtra is a potential zone of exotic zeolites like *stilbite*, *scolecite*, *natrolite*, *mesolite*, as well as their akines *okenite*, *cavensite*, and *apophyllite*. The extremely porous crystalline structured zeolites have a negatively charged honeycomb framework of micropores into

which molecules can be adsorbed for environmental decontamination, and to catalyse chemical reactions. Synthetic zeolites are most commonly used as catalysts in industrial processes like oil refining (for boosting the octane in gasoline, converting methanol to gasoline, and so on), chemical synthesis for pharmaceuticals, polymer, and other sectors. Zeolites have other beneficial uses like soil enrichment, animal feed, ion exchangers in the detergent industry, absorption of radioactive elements etc. Also, calcium-rich zeolites are known to inhibit naturally occurring chemical deterioration in black soils.

### GENESIS OF NATURAL ZEOLITES

Natural zeolites occur as an alteration product of glass of a volcanic or impact origin amorphous clay, and aluminosilicate gel. They replace crystalline materials such as nepheline, plagioclase, precursor zeolite and smectite. Also, they precipitate in cavities and veins from hot and cold solution. However, fine-grained glass fragments are most important raw material of natural zeolites for almost all types of occurrence, because of their high reactivity and similar chemical composition to certain zeolites. In all the cases, chemical reaction of volcanic ash and salt water result the formation of natural zeolites (Figure 1).

Several factors influence the formation of zeolite species. Chemical composition of the parent material, the host rock and temperature are the key factors of formation of different zeolite species (Table 1). For example, zeolites in alkali rocks are of "basic" species excepting analcime and faujasite, while those in acidic rocks are acidic and intermediate ones.



Table 1. Geological synthesis and occurrence of natural zeolites (Temperature shown is only an approximate)

Type of occurrence	Temperature	Zeolite species
Deep-sea sediments	4° – 50° C	Phillipsite ,clinoptilolite (analcime)
Earth surface weathering, Alkaline saline lake percolating groundwater (in basic tephra)	20° – 50° C	Phillipsite ,clinoptilolite, chabazite, erionite, mordenite, gismondine, faujasite, gonnardite, analcime (heulandite)
Percolating groundwater (in acidic tephra), Shallow burial diagenesis Low-temperature hydrothermal	25° – 100° C	Phillipsite, clinoptilolite, chabazite, erionite, mordenite, faujasite, analcime, thomsonite, mesolite, scole— cite, heulandite, stilbite, etc. except laumontite, wairakite and yugawaralite.
Deep burial diagenesis Moderate— temperature hydro— thermal	>100° C	laumontite, analcime,
Low-grade metamorphism High—temperature hydrothermal	>200° C	Wairakite, yugawaralite and analcime
Magmatic primary		analcime

(Source: Azuma Iijima, 1980)

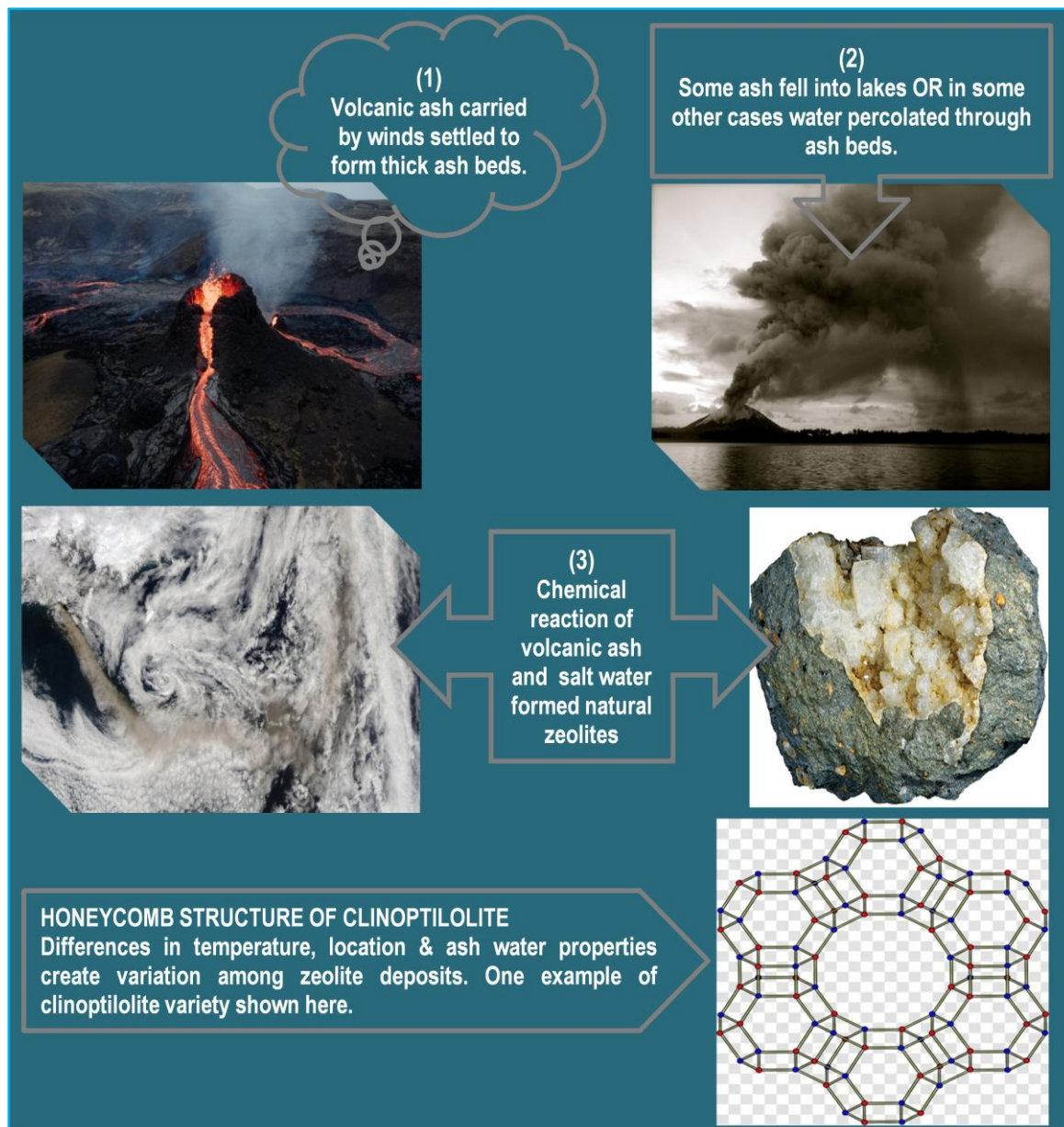


Figure 1. Diagram depicts the natural Zeolite formation processes



**STRUCTURE AND COMPOSITION OF ZEOLITES**

Zeolites are tectosilicates (three dimensional frameworks of  $\text{SiO}_4^{4-}$  tetrahedra in which all O's of each tetrahedron are shared with adjacent tetrahedra) (Figure 2&3). In zeolite structures, however, some of the quadrivalent Si is replaced by trivalent Al, giving rise to a deficiency of positive charge in the framework. This charge is balanced by monovalent and divalent cations, principally  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , elsewhere in the structure. Unlike quartz and feldspar, which have relatively dense and tightly packed three-dimensional framework structures, zeolite minerals have remarkably open three-dimensional framework structures, with void volumes of up to 50 percent reported in dehydrated species. Zeolites are categorised structurally based on the types of structural elements that make up the framework, such as rings or polyhedral. Different types of zeolites are given in Figure 4.

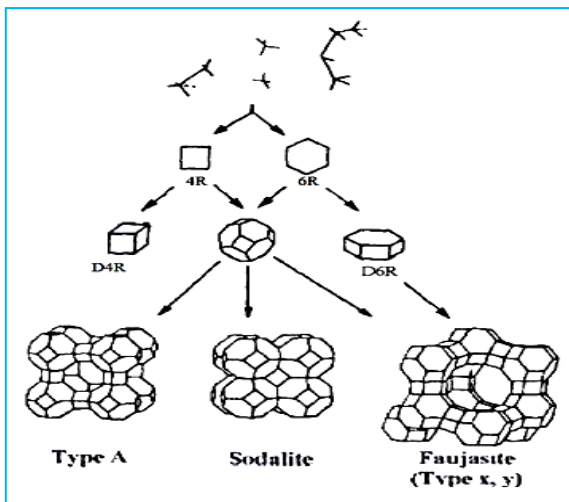


Figure 2. Structure of three different zeolites and their micropore systems

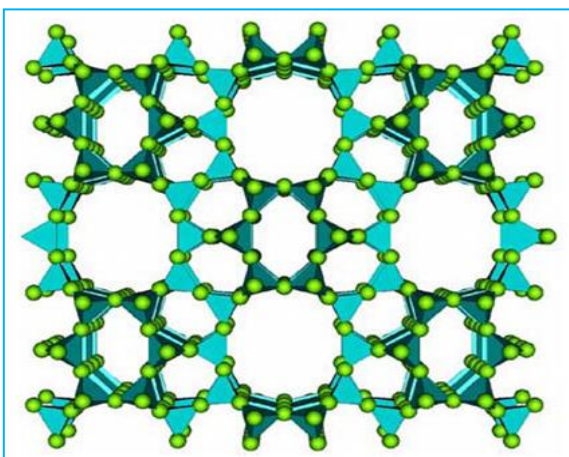


Figure 3. Chemical model of complex zeolites structure



Figure 4. Different types of zeolites

**IMPOTANCE OF ZEOLITE IN AGRICULTURE**

**Soil Nutrient Availability:** Because of their high porosity and CEC, zeolites can improve soil CEC, improving the ability of soils to collect and retain nutrients like ammonium ( $\text{NH}_4^+$ ) and potassium ( $\text{K}^+$ ). The CEC of naturally occurring zeolites ranges from 100 to 200 cmol/kg. In addition, zeolites can act as



slow-release agents for  $\text{NH}_4^+$  by reducing nitrification and subsequent nitrogen loss from urea. Huang and Petrovic (1994) found that addition of 10 percent (by weight) clinoptilolite to ammonium sulphate reduced ammonium leaching by 99 percent. Zeolite does not degrade over time and remains in the soil to help retain nutrients. As a result, by keeping beneficial nutrients in the root zone, its addition to the soil may significantly reduce water and fertilizer expenditures.

**Soil Health Enhancement:** Zeolites perform the role of a soil conditioner along with contributing to enhancing the soil health in many ways like improving soil water infiltration, strengthening soil structure, minimizing surface run off, soil erosion and nutrient leaching. According to Mpanga et al. (2020) zeolites play role in reducing greenhouse gases emission from soils. They illustrated various benefits of Zeolites incorporating the findings of Nahkli et al (2017) as given in Figure 5.

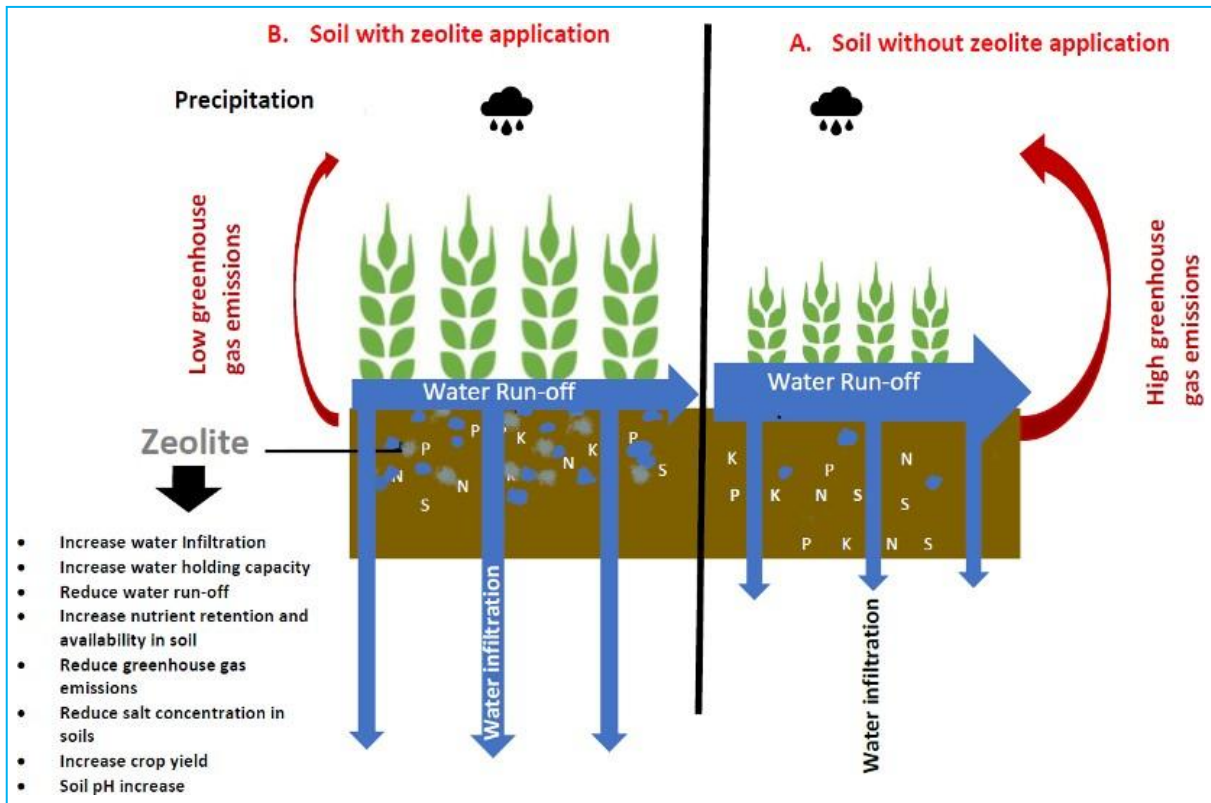


Figure 2. Benefits associated with using zeolites as a soil conditioner or amendment (Source: Mpanga et al. 2020)

**Environmental Pollution:** Application of zeolite leads to more efficient use of nutrient inputs and reduces environmental pollution of N & P in water bodies. Due to high CEC and porosity, zeolites absorb and trap green house gases such as methane and carbon dioxide. Application of zeolite helps to reduce ammonia gas emission during composting by preventing the conversion of  $\text{NH}_4$  to  $\text{NH}_3$ , which is a volatile greenhouse gas. Ramesh and Islam (2012) have found reduced loss of ammonium from zeolite mixed with cow manure at Ohio, USA.

**Physical Properties and Water Holding Capacity of Soil:** The high porosity of the zeolite structure helps in

improving the soil structure and aeration without blocking soil pores. Zeolites due to their porous structure can store water more than their weight and can act as reservoir by regulating the long-term water supply to crop plants. Zeolites also enhance water infiltration into soil, as well as irrigation water rewetting and lateral spread in the root zone. Xiubin and Zhanbin, (2001) reported that soil treatment with mordenite (zeolite species) having water holding capacity 121% (holding 1.21 times water of its own weight), increased soil water infiltration by 7-30% on a gentle slope and upto 50% on a steep slope. In another case study, Bigelow et al. (2001) found that mixing of clinoptilolite at a rate



of 10% by weight to a sandy soil increases 20% water holding capacity compared to untreated soil.

**Increases Yield:** The increased in yield of crops as a result of zeolite application with synthetic or organic fertilizers, which could be related to the benefits of improved soil structure, soil WHC, and improved soil nutrient conditions.

**Remediation of Contaminated Soil:** Application of zeolite increases the soil pH significantly, which helps in heavy metal adsorption on its surface, therefore, the solubility and bioavailability of heavy metals are ultimately reduced. Chen et. al. (2000) observed that the application of zeolite in soil significantly reduced the cadmium and lead accumulation in wheat.

### CONCLUSION

In the current scenario, agricultural area and production are rapidly dwindling, necessitating the usage of natural, non-toxic materials such as natural zeolite. Because of its structure and characteristics, it can be utilized as a slow releasing carrier of pesticide and fertilizers. Natural zeolite helps to improve soil's physical, chemical, and biological characteristics. As a result, zeolites may play an important role in agricultural input management in order to increase productivity, profitability, and sustainability. The knowledge obtained regarding the role of zeolites in preventing soil productivity loss and improving soil health enlightens us about their involvement in agricultural production.

### REFERENCES

Bassett, W.A. 1960. Role of hydroxyl orientation in mica alteration. *Bulletin of Geological Society of America* 71: 449-456.

Bogdanov, B., Georgiev, D., Angelova, K., and Yaneva, K. 2009. "Natural zeolites: Clinoptilolite Review," in International Science conference Economics and

Society Development on the Base of Knowledge, Stara Zagora.

Xiubin, H. and Zhanbin, H. 2001. Zeolite application for enhancing water infiltration and retention in loess soil. *Resour. Conserv. Recycl.*, 34, 45–52.

Huang, Z.T. and Petrovic, A.M. 1994. Physical properties of sand as affected by clinoptilolite zeolite particle size and quantity. *J. Turfgrass Manag.*, 1, 1–15.

Ramesh, K. and Islam, R. 2012. Zeolites regulate nitrogen release from manure amended soil. In Proceedings of the ASA, CSA and SSSA International Annual Meetings, Cincinnati, OH, USA, 21–24 October 2012.

Chen, Z.S.; Lee, G.J.; Liu, J.C. 2000. The effects of chemical remediation treatments on the extractability and speciation of cadmium and lead in contaminated soils. *Chemosphere*, 41, 235–242.

Iijima, A. 1980. Geology of natural zeolites and zeolitic rocks. *Pure & Applied Chemistry* 52, 2115 – 2130.

Fanning, D.S., Keramidas, V.Z., El-Desoky, and M.A., Micas. In: Dixon JB, Weed SB (ed) Minerals in Soil Environments. *Soil Sci Soc Am J. Madison, Wisconsin, USA*. 1989, pp551-634.

Mpanga, I.K., Braun, H., and Walworth, J. 2020. Zeolite application in crop production: Importance to soil nutrient, soil water, soil health and environmental pollution management. The University of Arizona, Cooperative Extension, az 1851.

Nakhli, S.A.A., Delkash, M., Bakhshayesh, B.E., and Kazemian, H (2017). Application of zeolites for sustainable agriculture: a review on water and nutrient retention. *Water Air Soil Pollution* 228(12), <https://doi.org/10.1007/s11270-017-3649-1>

\*\*\*