Introduction

A variety of crystalline microporous and mesoporous open framework materials have been synthesized and characterized over the past 50 years. Currently, open framework micro porous material finds applications primarily as shape or size selective adsorbents, ion exchangers, and catalysts. The recent progress in the synthesis of new crystalline micro porous material with novel compositional and topological characteristics promises new and advanced applications such as removal of radio nuclides, CO₂ sequestration & Hydrogen storage. The development of crystalline micro porous material started with the preparation of synthetic aluminosilicate Zeolite in late 1940s along with last two decades the open Frame pharmacosiderite analogue compounds such as Germano silicate, Titano silicate, Alumino germanate, Silico germanate were synthesized.
Now days Pharmacosiderite analogue compounds are equally important with Zeolites because of their high selectivity towards specific cations. Up to date the analogue compounds of pharmacosiderite are extensively applicable for the removal of radio nuclides. Basic Pharmacosiderite is a non-aluminosilicate molecular sieve with a framework composition $\text{KFe}_4(\text{OH})_4(\text{AsO}_4)_3\cdot6\text{H}_2\text{O}$ This compound crystallizes in the cubic space group, $P-43m$, with Unit cell length ‘$a’ \approx 7.98 \text{ Å}$. The pharmacosiderite consist of FeO$_6$ octahedra and AsO$_4$ tetrahedra connected to each other to form a three-dimensional network of channels. The pore has 8 membered ring openings with alternate arsenic tetrahedra and iron octahedra. Each pore is occupied by charge neutralizing cations and water molecules.

The octahedral and tetrahedral sites can be replaced by other elements and in fact, a compound with aluminum in place of iron occurs naturally. Although Alumino-pharmacosiderites are sometimes improperly termed ‘zeolitic germanate’ (Zemann J. 1959), they are in fact nonzeolitic molecular sieves built up from octahedral and tetrahedral building units connected to each other to form a 3D network of 8-ring pores with a diameter of ca. 4.3 Å. This class of micro porous solids, which naturally occur as iron arsenates (Proust, 1790), shows cation exchange properties, on the other hand, some synthetic analogues undergo facile ion exchange of both cations and anions. Titano silicate & Germanium substituted silicates having high selectivity for Cs giving potential for the removal of $^{137}\text{Cs}$ from nuclear waste water has also been reported (Behrens E.A.,(1998). The ionic conductivity and humidity-sensing properties of pharmacosiderite-like materials have been the topic of another study (Dianlai Yang, 2009). To date, there is a large family of pharmacosiderite analogues with different framework compositions, most of which retain the cubic space group $P-43m$, due to the ease of isomorphous substitution of octahedral Fe and tetrahedral As by Ti or Ge and Si or Ge, respectively, for this
class of micro porous materials (Clearfield, (1998). Also, pure germanate pharmacosiderites with cubic, body-centered cubic, and rhombohedral symmetries have long been synthesized (Geoffrey M.(1999). However, no synthetic efforts have thus far been devoted to their alumino silicate & zirconium silicate pharmacosiderites.

To date, there are many papers on the synthesis of the pure germanate analogues of pharmacosiderite, first using NH$_4^+$ and later on with various other cations. For example, Feng,Greenblatt(1992) reported the synthesis of germanate pharmacosiderite in the presence of an alkali metal cation ranging from Li$^+$ to Cs$^+$. They failed to directly synthesize the Li$^+$ form and thus prepared it by cation exchange from the Na$^+$ form. Furthermore, all of their germanate materials were characterized to have the cubic space group $P-43m$ and thus no dependence of the crystal symmetry of the crystallized product on the type of alkali metal cations employed in pharmacosiderite synthesis was observed.

**Literature Review**

Pharmacosiderite is a hydrated ferric arsenate, has chemical formula KFe$_4$(AsO$_4$_3(OH)$_4$.6H$_2$O and molecular weight of 873.38 g/mol. It consists of the elements arsenic, iron, potassium, oxygen and hydrogen. Pharmacosiderite has an isometric crystal system, with yellowish green, sharply defined cube crystal. Its crystals are doubly refracting and exhibit a banded structure in polarized light. It is found in abundance in Cornwall, Hungery and the U.S. state of Utah. When it was first discovered, pharmacosiderite was known as cube ore. The present name, given by J. F. L. Haussmann in 1813, is made up of the Greek words for arsenic and iron, the two most significant elements, *Farmakon* means poison, which is related to arsenic and *sideros* means iron.
Pharmacosiderite is a hydrated iron arsenate mineral which has been known since 1790. DANA'S System gives its chemical composition as $\text{Fe}_3(\text{AsO}_4)_2(\text{OH})_3$. 5$\text{H}_2\text{O}$, and assigns it to space group $P-43m$ with 11/2 formula units to a unit cell whose edge is $a = 7.94$ kX. Pharmacosiderite was first described by Proust in 1790. Since then, many chemical formulas have been assigned to this compound. In 1824 Berzelius’ chemical analysis suggested the composition $\text{Fe}_8\text{As}_6\text{O}_{21}.15\text{H}_2\text{O}$. Seventy-six years later E. G. J. Hartley (1900) made new analyses and proposed the formula $2\text{FeAsO}_4.\text{Fe}(O, \text{K})_3.5\text{H}_2\text{O}$. However, in 1928 Heide reported that the potassium, instead of being a substituent of the hydrogen should take a place in the channels of the structure together with the zeolitic water.

The first serious attempt to elucidate the crystal structure of pharmacosiderite, together with its real chemical formula, was made in 1937 by Hagele and Machatschki. The structure proposed by Hagele and Machatschki for alumino pharmacosiderite and this pharmacosiderite was re-examined in 1948 by Zemann with special regard to the iron compound.

Table: 1 Comparison of the structures for pharmacosiderite proposed by Hagele and Machatschki and by J. Zemann

<table>
<thead>
<tr>
<th>Hagele and Machatschki</th>
<th>Zemann</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Fe(or 5A) in 1(a) + 4(e)</td>
<td>4Fe in 4(e)</td>
</tr>
<tr>
<td>3As in 3(c)</td>
<td>3As</td>
</tr>
<tr>
<td>12(O) in 12(i)</td>
<td>12(O) in 12(i)</td>
</tr>
<tr>
<td>6(OH) in 6(f)</td>
<td>4(OH) in 4(e)</td>
</tr>
<tr>
<td>H$_2$O molecules in the channels of the structure</td>
<td>4(H$_2$O) in 4(e)</td>
</tr>
<tr>
<td>positions not specified.</td>
<td>3(H$_2$O) in 3(c)</td>
</tr>
</tbody>
</table>
Pharmacosiderites are an excellent example for a nontetrahedral framework structure with obvious zeolitic properties. Like the Zeolite, it is extremely tolerant of exchanges of its pore-filling. In addition the constituent cations of the framework can be very variable. All this makes them similar to some of the tetrahedral zeolitic frameworks. In fact numerous additional pharmacosiderites with other chemical compositions have been prepared in the meantime (Table 2). The octahedral sites can be occupied by Al, Fe, Ge, Mo or Ti, the tetrahedral sites by As, Ge, P or Si. The nonframework cations can be Ag, Ba, Cs, H, K, Li, Na, NH$_4$, Pb, Rb and Tl. Various cation-exchange experiments have been performed on natural (MUTTER et al., 1984) and synthetic (NENOFF et al., 1994) pharmacosiderite type compounds. The titanosilicate analog of pharmacosiderite was in addition exchanged with Mg and Ca, and furthermore used to remove trace amounts of Cs and Sr, which makes it interesting for the removal of radioactive isotopes of these elements (DYER et al., 1999). Three additional minerals have been found to belong to the pharmacosiderite group.

Table 2: Pharmacosiderite analogue compounds presently known

<table>
<thead>
<tr>
<th>Location</th>
<th>Chemical elements or groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octahedral site</td>
<td>Al, Fe, Mo, Ti</td>
</tr>
<tr>
<td>tetrahedral site</td>
<td>As, Ge, P, Si</td>
</tr>
<tr>
<td>pore filling</td>
<td>Ag, Ba, Ca, Cs, H, K, Mg, Rb, Sr.</td>
</tr>
</tbody>
</table>

**Germanium Pharmacosiderites**

Germanium Pharmacosiderites are sometimes improperly termed ‘zeolitic germanate’, they are in fact nonzeolitic molecular sieves built up from octahedral and tetrahedral building units.
connected to each other to form a 3D network of 8-ring pores with a diameter of ca. 4.3 Å. this class of compound shows cation exchange properties, some synthetic analogs undergo facile ion exchange of both cations and anions (Clearfield A.,1995). A high selectivity for Cs⁺, giving potential for the removal of ¹³⁷Cs from nuclear waste water, has also been reported by Behernes E., A.Clearfield (1998). To date, there is a large family of pharmacosiderite analogs with different framework compositions, most of which retain the cubic space group $P-43m$, due to the ease of isomorphous substitution of octahedral Fe and tetrahedral As by Ti or Ge and Si or Ge, respectively, for this class of microporous materials. Also, pure germanate pharmacosiderites with cubic, body-centered cubic, and rhombohedral symmetries have long been synthesized. Geoffrey M. Johnson (1999) find novel routes to synthesis of germanium containing Zeeolites. However, no serious synthetic effort has thus far been devoted to their Aluminogermanate, Zirconium germanates and silicate pharmacosiderites analogue compounds.

Pharmacosiderite is a mineral found naturally based on iron and arsenic. Here Germanium pharmacosiderite refers to the germanium analogue of pharmacosiderite that is produced in some of synthesis. In Ge-pharmacosiderite the entire tetrahedra are shared between the Ge10 clusters as seen in. It can be described as a body-centered packing of the Ge10-clusters.

The attempts are to synthesise Ge-substituted pharmacosiderites and its application to remove radioactive isotopes from nuclear waste (Eulenberger G. 1961). Recent advances in the field of zeolite synthesis have established that the introduction of heteroatoms such as Li, Be, B, Zn, and Ge into silica frameworks during the crystallization process is another rational strategy in the hunt for previously unknown topologies. This is also the case for Ga, the element right below Al in its group of the periodic table. Indeed, the discovery of several novel gallosilicate zeolites including TsG-1/ECR-9/TNU-1 (frame-work type CGS), ECR-34 (ETR) and TNU-7
(EON), (Warrender S.J., 2005) has demonstrated that despite the close chemical similarity between Ga and Al, the structure-directing ability exerted by the former at low-silica compositions can be substantially different from that of the latter when the concentration of trivalent lattice-substituting elements in the synthesis mixture, together with the type and concentration of alkali metal cations, is properly selected. As a extension of previous studies on the synthesis of low-silica gallosilicate zeolites without the aid of organic structure-directing agents (SDAs) in alkaline media on the other hand, we have taken interest in the search for new zeolitic structures at germanate-based compositional domains and then performed a number of syntheses using Ge as a tetravalent, tetrahedral lattice-substituting element. Contrary to desire, however, the crystallized products were found to be mostly pharmacosiderite analogs, while three-dimensional (3D) open frameworks with tetrahedral Ge atoms (i.e., true germanate zeolites) were scarce. Although pharmacosiderites are sometimes improperly termed ‘zeolitic germanates’, they are in fact nonzeolitic molecular sieves built up from octahedral and tetrahedral building units connected to each other to form a 3D network of 8-ring pores with a diameter of ca. 4.3 Å. While this class of microporous solids, which naturally occur as iron arsenates with a typical framework composition $\text{KFe}_4(\text{OH})_4(\text{AsO}_4)_3.6\text{H}_2\text{O}$, shows cation exchange properties, some synthetic analogs undergo facile ion exchange of both cations and anions. A high selectivity for Cs+, giving potential for the removal of $^{137}\text{Cs}$ from nuclear waste water, has also been reported. To date, there is a large family of pharmacosiderite analogues with different framework compositions, most of which retain the cubic space group P-43m, due to the ease of isomorphous substitution of octahedral Fe and tetrahedral As by Ti or Ge and Si or Ge, respectively, for this class of microporous materials. Also, pure germanate pharmacosiderites with cubic, body-centered cubic, and rhombohedral symmetries have long been synthesized. However, no
synthetic effort has thus far been devoted to their aluminogermanate analogues. Hailian L. (1998), had synthesised Porous Germanates Structure of Ge\textsubscript{7}O\textsubscript{14}.[(CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2}]\textsubscript{3}(H\textsubscript{2}O).

There are no attempts going on to synthesise Aluminiu, Zirconium silicate and there modified compounds. So my emphasis is to synthesise & characterize these pharmacosiderite analogue compounds. These materials will be useful for removal radionuclides of hydrogen storage or for CO\textsubscript{2} sequestration.

**Alumino Germanate Pharmacosiderite**

Jiho Shin (2009) and his co-workers synthesize the aluminogermanate pharmacosiderites and studied there structures. This study concludes, Aluminogermanate pharmacosiderites can crystallize hydrothermally as primitive cubic \(P-\overline{4}3m\), rhombohedral \(R3m\), and body-centered cubic \(I23\) phases, depending on the type of alkali metal ions in the synthesis mixture. For example, replacement of NaOH by KOH and LiOH under the conditions where the crystallization of the rhombohedral NaAlGe-Pha material proved to be highly reproducible yielded body-centered cubic KAlGe-Pha and primitive cubic LiAlGe-Pha materials, respectively, but not any zeolitic phase with all-tetrahedral Ge atoms. When RbOH is used as an alkali metal cation source, in addition, the body-centered cubic RbAlGe-Pha material, together with an amorphous phase, was the product obtained after 14 days of heating at 150\(^\circ\)C. By contrast, the use of CsOH gave a mixture of the aluminogermanate analog of analcime. The crystal structures of the aluminogermanate analogues determined by Rietveld analyses of synchrotron X-ray diffraction data. The materials prepared here are further characterized by using elemental and thermal analyses, scanning electron microscopy, high-temperature X-ray diffraction, IR and 27-Al MAS NMR.

**Titanosilicate Pharmacosiderites**
A series of titanosilicate, germanium-substituted titanosilicate pharmacosiderites, and titanate inorganic ion exchangers were developed by the Department of Chemistry at Texas A&M University in conjunction with Allied Signal and the Pacific Northwest National Laboratory (PNNL) for the selective removal of strontium or cesium from different contaminated aqueous defense wastes and groundwater. Over the past 50 years, the Hanford nuclear plant located in Washington State accumulated over 65% of nation’s High-Level radioactive Waste (HLW) resulting from chemical extraction processes for the production of nuclear weapons grade $^{239}$Pu. Recent reports have indicated that the titanosilicate pharmacosiderite exchanger is selective for low concentrations of Sr$^{2+}$ and Cs$^+$ in the presence of ppm levels of Na$^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$ cations at neutral pH.7.

In 1990, Chapman and Roe prepared a number of titanosilicate analogues of pharmacosiderite, including Cs, Rb and exchanged protonated phases. Harrison et al. (1995) reported structure of Cs$_3$H[Ti$_4$O$_4$(SiO$_4$)$_3$](H$_2$O)$_4$. Behrens et al. (1996), Behrens and Clearfield (1997) and Dadachov and Harrison (1997) provided data on preparation, structures and properties of A$_3$H[Ti$_4$O$_4$(SiO$_4$)$_3$](H$_2$O)$_n$ (A = H, Na, K, Cs). Structures and ion-exchanged properties of HA$_3$[M$_4$O$_4$(XO$_4$)$_3$](H$_2$O)$_4$ (A = K, Rb, Cs; M = Ti, Ge; X = Si, Ge) were reported by Behrens et al. (1998). These compounds were considered as perspective materials for the selective removal of Cs and Sr from waste water solutions. However, no natural titanosilicates with pharmacosiderite topology have been reported so far. In this article, report for the first time occurrence of four pharmacosiderite-type titanosilicates and their cation-exchange properties.

**Zirconium, Aluminium silicate Pharmacosiderite**

There were no efforts taken to synthesize the Alumino silicate and zirconium silicate pharmacosiderites. Therefore my emphasis is to synthesize Aluminum and Zirconium silicate...
pharmacosiderite by hydrothermal synthesis and are characterized by XRD, EDAX, SEM techniques.

**Objectives of the proposed work:**

- Hydrothermal synthesis of Zircono, Alumino Silicates having Pharmacosiderite topology.
- Hydrothermal synthesis of titanium substituted Zircono, Alumino Silicates.
- Characterization of these compounds by XRD, EDAS, DTA and SEM.
- To study the Ion exchange property.
- To study the CO$_2$ Adsorption on these materials.

**Hypothesis**

The requirements of the present day materials can be obtained by two ways. First is by synthesizing the materials with different topology or crystal structure and second way is by modifying the present materials. Pharmacosiderite materials show wide flexibility of framework composition and also with wide varieties of exchangeable cations.

**Plan of Work**

The work plan envisaged the synthesis of various analogues Pharmacosiderite materials having composition A$_4$Si$_3$B$_4$O$_{16}$nH$_2$O (A= Na, Cs, Sr, K B= Al & Zr) with metal ion substitution by
hydrothermal synthesis. The various composition gels will be prepared by hydrothermal synthesis.

This study is divided into three parts

PART I: Synthesize the various phases having different topology of Zr and Al by hydrothermal synthesis

Pharmacosiderite mineral : \( \text{KFe}_4(\text{OH})_4(\text{AsO}_4)_3.6\text{H}_2\text{O} \)

Zirconium silicate pharmacosiderite : \( \text{A}_4(\text{ZrO})_4(\text{SiO}_4)_3.6\text{H}2\text{O} \)  (Where A= Na,K,Li)

Aluminium silicate pharmacosiderite : \( \text{A}_4(\text{AlO})_4(\text{SiO}_4)_3.6\text{H}2\text{O} \)  (Where A= Na,K,Li)

PART II: Characterization of synthesized material by using XRD,SEM & DTA technique.

PART III: Study the applications to ion exchange, catalytic property, \( \text{CO}_2 \) adsorption capacity etc of these synthesized compounds.

PART I: Synthesize the various phases having different topology of Zr and Al by hydrothermal synthesis

**Methodology**

Hydrothermal synthesis of pharmacosiderite analogue compounds

Experimental Procedure

1) Preparation of gels: Several precursors with general composition \( x\text{Na}_2\text{O}:2\text{Al}_2\text{O}_3:3\text{SiO}_2:n\text{H}_2\text{O} \) and \( x\text{Na}_2\text{O}:2\text{Zr}_2\text{O}_5:3\text{SiO}_2:n\text{H}_2\text{O} \) are prepared (Where \( x=4 \) to 10 moles and \( n=150 \) to \( 200 \) mol)

2) The aluminum isopropoxide & fumed silica mix in the proportion \( 2:3 \) mole with \( 15 \) ml water & stirred for \( 8 \) hr. by using magnetic Stirrer for forming homogeneous gel.

3) Then \( 4-10 \) mol NaOH solution is add drop wise with continues stirring for an hr.
4) This gel is poured in Teflon beaker of capacity 100 ml and kept in acid digester bomb.

5) The acid digester bomb is kept in Oven at Temp. 250 -270\(^0\)C for 14 days.

6) The resulting compound is washed with water four to five times and finely by ethanol.

7) It is kept for drying at 80\(^0\)C for one hr.

PART II: Characterization of synthesized material by using XRD,SEM & DTA technique.

1) XRD: Structural determination, Phase composition

2) EDAS: Percentage composition of compounds

3) DTA/TGA : Determination of free water and structural water

4) SEM: Determination of particle size and surface morphology

PART III: Study the applications to ion exchange, catalytic property, CO\(_2\) adsorption capacity etc of theses synthesized compounds.

REFERENCES


