Stability of Jarosite on Mars

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Abstract

Using first principles density functional theory, we have studied the effect of Na doping at K-sites of Jarosite. Previous theoretical studies show that $KFe_3(SO_4)_2(OH)_6$ will decompose into yavapaiite ($KFe(SO_4)_2$), hematite(Fe_2O_3) and water (H_2O) under Martian conditions beyond 18C. However, several studies indicate that Martian Jarosite contains a significant amount of Na doped at K sites in the jarosite crystal structure. Therefore, in this study we have investigated the effect of Na at K-sites of jarosite as a function of pressure. Our calculations find that Na increases the stability field of jarosite. Further the relative stability of natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) as compared to pure K-end member of jarosite ($KFe_3(SO_4)_2(OH)_6$) increases as pressure is increased.

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1. Introduction

Mars is the second most exciting planet for human beings and the fourth largest planet from the Sun. It is also the furthest planet from the Sun among the rough terrestrial planets that make up the group of terrestrial planets. In this planetary family, Mercury is the only planet that is smaller than Mars. The surface gravity of Mars is 3.72 m/s^2, which is 37.6% of Earth's gravity. Compared to land (101 kPa), the current ambient pressure coefficient is low (~ 0.6 kPa) and the atmosphere is mostly carbon dioxide (95%). The angle of inclination of Mars is 25° and may have changed several degrees in recent years (Laskar et al., 2004).

The polar ice caps of Mars that can be detected from the Earth are mainly water ice. In addition, if we look at the topography of Mars, there are valley- like shapes from high land area to low land area which indicate that fluid did flow on its surface in the past. Such findings have aroused the curiosity of mankind and ever since then man has been in search of ways in which the surface of Mars could be made worthy of sustaining life. (for example, Des Marais, 2010). Mars has a normal orbit around the sun which is 50 times more than Earth and is the lone planet outside of the Earth. It therefore lies in the possible sustainable area of the nearby planet group (Kopparapu et al., 2013).

After the Earth, Mars is the only planet in our solar system that has maximum possibilities of life or making life possible in the future, due to this reason, exploration of Mars officially started in the 1960s. From that point till now, we have gathered much information about Mars. In these discoveries, we also got to know about the presence of Jarosite minerals on Mars.

Jarosite, a ferric-potassium hydroxide sulfate [$KFe_3(SO_4)_2(OH)_6$], was firstly guessed to be a typical mineral on Mars by Burns despite an uncommon occurrence on the Earth. In 2004 a wide range of jarosite at 35 Meridiani Planum was accounted for by the Opportunity rover; Meridiani Planum is a place on Mars where the Opportunity rover landed. Jarosite content is about 10% in the outcrop at the Meridiani Planum, affirming Burns' prediction, yet the topographical setting where jarosite was found - in fine grained residue inside layered developments (of hematite) was hard to decipher. From that point onwards, the mineral jarosite has been discovered over and over again on the surface of Mars and has been viewed as a proof of the fact that water was indeed present on the Mars surface. This is because on the surface of our Earth, jarosite appears as an after-effect of low-temperature acidic-oxidative reaction of iron-bearing minerals in the presence of restricted water.

The long-term preservation of jarosite requires dry conditions because prolonged water action brings about its disintegration/dissolution. Therefore, the presence of jarosite on Mars is thought to be indicative of the fact that the weathering fluid, i.e., water was active on Mars for a geologically short time interval.

Figure 1. Image of Jarosite Mineral found on Earth

Previous research on jarosite indicates that it has a restricted stability field and is precipitated from profoundly acidic (pH is less than 3), oxidizing watery liquids in a sulfur-bearing framework [e.g., Noble and Palmer, 1996; Bigham et al., 1996]. These outrageous conditions are normal in corrosive mine wastes (acid mine drainages) [e.g., Chapman et al., 1983; Alpers et al., 1989, 1992] yet are generally not effortlessly acknowledged in regular earthbound circumstances, consequently restricting the scope of conditions in which jarosite can be formed and preserved on Earth.

Of the last mentioned, the most well-known event of jarosite is in the oxidized gossans of ore deposits, where it is formed through the action of strong (pH is less than 3) sulfuric acid in groundwater which leads to the reaction of pyrite with gangue minerals and divider rock in the ore deposits [Alpers et al., 1994; Bigham and Nordstrom, 2000; Crowley et al., 2003; Herrmann et al., 2001; Nordstrom and Alpers, 1999]. Pyrite oxidation in coal, shale, or muds may lead to the formation of jarosite [Oliveira et al., 2012; Silva et al., 2012; Rothstein, 2006].

Jarosite may also be related to the aqueous stores/hydrothermal deposits, where it forms a hypogene mineral, such as in Yellowstone Public Park hot spring deposits [Allen and Day, 1935], Japan [Fujimitsu and Mia, 2012], and Indonesia [Bernard and Delmelle, 2000]. Indeed, acidophilic microbes have been blamed for creating outrageous conditions by producing mineral biosignatures such as goethite, jarosite, and hematite, as seen in Ro Tinto (Iberian Pyritic Belt) [Amils-et-al., 2007].

Different ideas have been presented, for example, to explain how jarosite-shaping conditions could have been achieved on Mars. For example, Clark and Baird [1979], Settle [1979] and Consumes [1987] recognized that volcanic degassing is an important source of sulfur, which is consolidated into a solid in the Martian weathering layer through fluid alteration or gaseous interaction. [Elwood Madnetal. [2004]; Baning-et-al., 1997; Catlin, 1999; Bibringetal., 2006; Marionetta, 2003; Farquharetal., 2000; Toscaetal., 2004]. Local heating of an ice-bearing crust produced fluid(aqueous), sulfide-rich subsurface waters that accelerated/precipitated pyrite in close surface despondencies, which then went through aqueous oxidation to create jarosite and other hydrous sulphates, according to Zolotov and Shock [2005]. Various articles, including Chevrier-et-al. [2004, 2006], Poulet-et-al. [2008], and Dehouck-et-al. [2012], have proposed that the hydrous sulphates are formed by the oxidation of sulphides. A large portion of these hypotheses are mostly based on the foundations of natural jarosite presence on Earth.

Therefore, identifying jarosite-containing terrestrial locations is important because they help narrow the range of environments where minerals may form, some of which may be used as analogues of Martian surface processes.

1.2 Previous work

Decomposition of Jarosite(K- endmember Jarosite):-

$KFe_3(SO_4)_2(OH)_6$	$\Rightarrow$	$KFe(SO_4)_2$	+	Fe_2O_3	+	$3H_2O$
Jarosite		Yavapaiite		Hematite		Water vapour

Thermodynamic data that is used to calculate the stability of jarosite in previous work:-

Compound	ΔH_f^O (kJ mol−1)	S^o (J mol−1 K−1)	ΔS_f^o (J mol−1 K−1)
$KFe_3(SO_4)_2(OH)_6$	-3829.6 ± 8.3 [a]	388.9 [b]	-1648.8 [a]
$KFe(SO_4)_2$	-2042.8 ± 6.2 [c]	224.7 ± 5.0 [c]	-751.9 ± 1.0 [c]
Fe_2O_3	-826.2 ± 1.3 [d]	87.4 ± 0.2 [d]	
$3H_2O$	-241.8 ± 0.0 [d]	188.8 ± 0.0 [d]	

a (Drouet and Navrotsky, 2003)

b (Stoffregen, 1993).

c (Forray et al., 2005).

d (Robie and Hemingway, 1995).

Thermodynamic estimations show that under the low mean total air pressure (6.76 mbar) on Mars (Haberle et al., 1999), where the partial-pressure of H_2O is $\sim 2.5 \times 10-3$ mbar, the balance deterioration of jarosite to yavapaiite, water vapour and hematite (Eq. (1)) happens at $+18\ ^oC$. At the Opportunity arrival site at Meridiani Planum, where jarosite was recognized (Klingelhöfer et al., 2004), the rover estimated temperatures somewhere in the range of -91 and $+148\ ^oC$ (Smith et al., 2004) with an error of estimation under $O.5^{o}C$. The normal surface temperature at the equator is around $-54^{o}C$ (Kieffer et al., 1977).

Taking into account that the sedimentary layered developments have low thermal conductivity, it is sensible to consider any irregular fleeting temperature over $0^{o}C$ to influence just the surface layers only. For layered deposits, estimations show that the temperature can rapidly diminish by $60\ ^{o}C$ in the initial 50 cm (Mellon et al., 2004). In this manner we infer that jarosite is inside its thermodynamic stability field under present surface situations on Mars.

Photo-decomposition of sulfates by exceptional solar-ultravoilet radiation offers another potential decay pathway. Test recreation of the photodecomposition of carbonates and sulfates (Mukhin et al., 1996) shows that solar-ultravoilet radiation is surely ready to break down sulfates and may raise the temperature of the minerals by around $25^{o}C$. Such an ascent of temperature may bring jarosite to its deterioration boundary, however just in oddly warm areas. This thermal or/and photocatalysed deterioration will most likely be restricted to a very thin surface layer, and the disintegration items (yavapaiite and iron oxide) on the jarosite surface would presumably control decay beneath the surface. In this way photodecomposition is most likely not a significant component for breakdown of jarosite on the martian surface.

The above thermodynamic estimations were finished considering that the jarosite present on Mars is the unadulterated potassium endmember. The quadrupole splitting powers of Mössbauer spectra recorded by Opportunity rover show that the jarosite presumably is a K/Na type (Klingelhöfer et al., 2004). This finding is additionally steady with the K and Na bounty announced by the rover's alpha molecule X-beam spectrometer (Rieder et al., 2004). Be that as it may, the real K/Na proportion in the martian jarosite isn't known. The thermodynamic impacts of this partial sodium replacement or dehydratation response can't be determined because , however the energetics of K/Na replacement in jarosite are surely understand (Drouet et al., 2004,Drouet and Navrotsky, 2003;), those in the yavapaiite stage have not been calculated. The jarosite mineral derived from the Opportunity rover investigations is subsequently sensible on both thermodynamic and dynamic grounds. These jarosite minerals continue to the current day since they are thermodynamically steady, yet their underlying development probably required wetter/moist conditions for successful mass transports and crystallizations.

1.3 My work

From the previous works , we got to know that maybe the Jarosite on Mars doesn't contain only potassium end member jarosite. Some K is replaced by Na in Jarosite, maybe this led to decomposition of Jarasite at lower temperature for average atmospheric pressure on Mars.

In our studies, we are going to find out the effect of the pressure only. We are going to calculate the enthalpy of formation of each of the phases.

Now, we have two equations to study the effect of sodium on the stability of Jarosite on Mars.-:

$$KFe_3(SO_4)_2(OH)_6 \Rightarrow KFe(SO_4)_2 + Fe_2O_3 + 3H_2O$$

Jarosite Yavapaiite Hematite Water vapour

$$NaFe_3(SO_4)_2(OH)_6 \Rightarrow NaFe(SO_4)_2 + Fe_2O_3 + 3H_2O$$

Natro-jarosite Eldfellite Hematite Water vapour

First reaction is Jarosite breakdown into Yavapaiite, Hematite and water vapour.
So there change in enthalpy will be :-

$$\Delta H_1 = \Delta H_{Yavapaiite} + \Delta H_{Hematite} + \Delta H_{Water\ vapours} - \Delta H_{Jarosite}$$

Where ΔH_1 is dissociation enthalpy of Jarosite into Yavapaiite, Hematite and water vapour.

Here, positive value of ΔH_1 indicates Jarosite would break down into Yavapaiite, Hematite and Water vapour and negative value of ΔH_1 indicates Jarosite is stable and will not break down into Yavapaiite, Hematite and Water vapour in the absence of temperature effect.

Similarly,

For the second reaction is Natrojarosite breakdown into Eldfellite, Hematite and water vapour.
So there change in enthalpy will be :-

$$\Delta H_{2} = \Delta H_{Eldfellite} + \Delta H_{Hematite} + \Delta H_{Water\ vapours} - \Delta H_{Natrojarosite}$$

Where ΔH_{2} is dissociation enthalpy of Natrojarosite breakdown into Eldfellite, Hematite and water vapour.

Here, positive value of ΔH_{2} indicates Natrojarosite would break down into Eldfellite, Hematite and Water vapour and negative value of ΔH_{2} indicates Natrojarosite is stable and will not break down into Eldefellite, Hematite and Water vapour in the absence of temperature effect.

After getting ΔH_{1} and ΔH_{2} values now we are going to plot ΔH_{1} - ΔH_{2} v/s pressure which will indicate whether the natrojarosite is more stable or not.

2. Methodology

All matter is made out of the atom and atoms are made out of a positively charged nucleus and out of many negatively charged electrons, such that the net charge on the system is zero. Therefore any material can be considered to be a collection of interacting electrons and ions. The exact theory for such a system is based on solving the quantum mechanical Schrodinger equation which seemed different for a many electron system.

Hohenberg–Kohn proved that it was indeed possible to develop such a theory for a many particle system. They proposed two remarkably strong theorems in this regard.

1. There is a one to one correspondence between the ground state density of a N- electron system and the external potential acting on it.
2. The density that minimizes the total energy is the exact ground state.

3. Crystal structures

JAROSITE

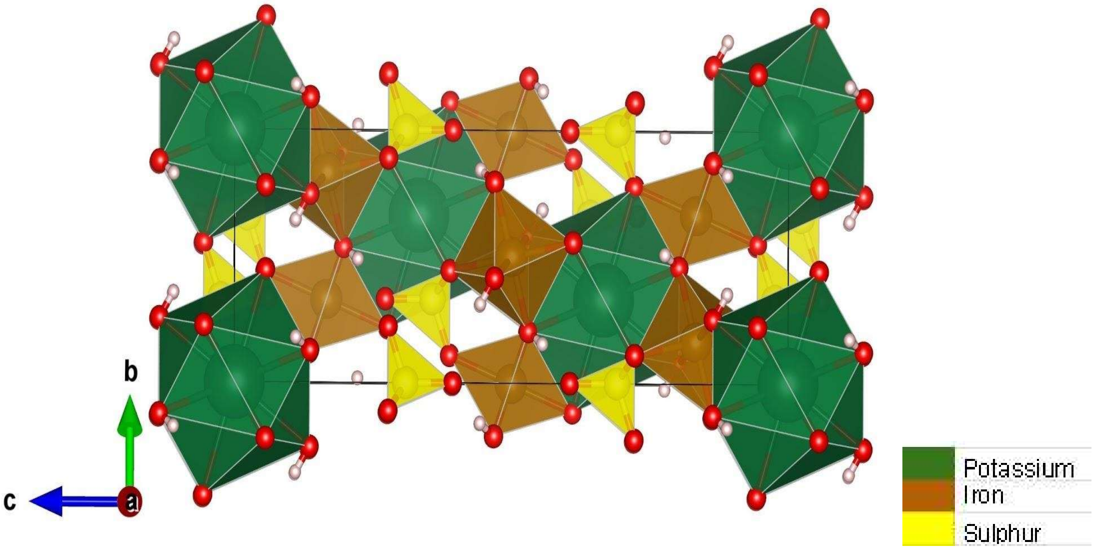

Figure II . Jarosite crystal structure

Jarosite crystallizes into rhombohedral form ($R\bar{3}m$) .

The lattice parameters of Jarosite crystals are are a = 7.33009 Å, b = 7.33009 Å, c = 17.13790 Å and $\boldsymbol{\alpha}=\boldsymbol{\beta}=90^\circ$, $\boldsymbol{\gamma} = 120^\circ$

Above figure is a crystal structure of Jarosite and the structure presented there is projected into a bc plane.

The green is Potassium in the crystal structure and it is at 12- fold coordination.
The brown is Fe in the crystal structure and it is at 6 fold coordination
The yellow is sulphur in the crystal structure , it is at 4 fold coordination
Red ball represents the oxygen atom and white ball represents the Hydrogen atom in the crystal structure .

YAVAPAIITE

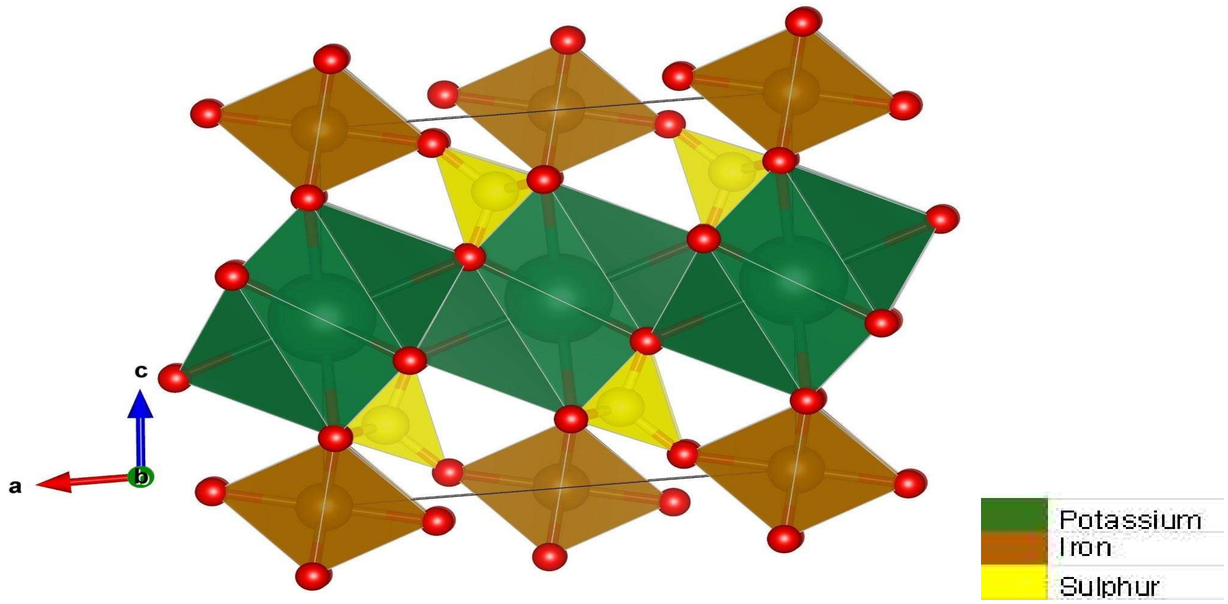

Figure III . Yavapaiite crystal structure

Yavapaiite crystallizes into a monoclinic form(C2/m).

The lattice parameters of yavapaiite crystal structure are a = 8.1520 Å b = 5.1530 Å , c = 7.877Å, and $\boldsymbol{\alpha}$=90° , $\boldsymbol{\beta}$=94.9°, $\boldsymbol{\gamma}$ = 90°.

Above figure is a crystal structure of Yavapaiite and the structure presented there is projected into a ac plane.

The green colour in the crystal structure is Potassium and it is at 8 fold coordination.
The brown color in the crystal structure is Iron and it is at 6 fold coordination
The yellow colour in the crystal structure is sulphur, it is at 4 fold coordination
Red ball in the crystal structure represents an oxygen atom.

NATROJAROSITE

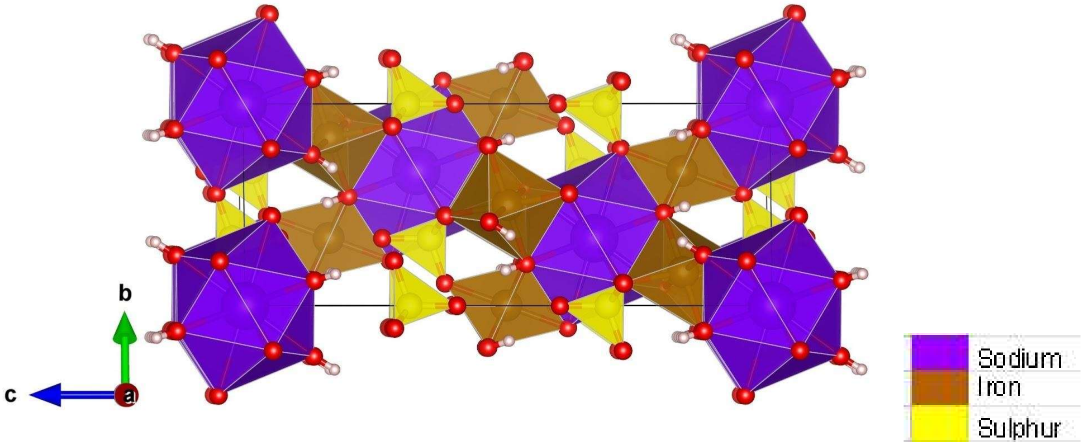

Figure IV . Eldfellite crystal structure

Natrojarosite crystallizes into rhombohedral form ($R\bar{3}m$) .

The lattice parameters of Natrojarosite crystals are a = 7.3101 Å , b = 7.3101 Å , c = 16.7658 Å, and $\boldsymbol{\alpha}$=$\boldsymbol{\beta}$=90° , $\boldsymbol{\gamma}$ = 120°

Above figure is a crystal structure of natrojarosite and the structure presented there is projected into a bc plane.

The Purple is sodium in the crystal structure and it is at 12- fold coordination.
The brown is Fe in the crystal structure and it is at 6 fold coordination
The yellow is sulphur in the crystal structure , it is at 4 fold coordination
Red ball represents the oxygen atom and white ball represents the Hydrogen atom in the crystal structure.

ELDFELLITE

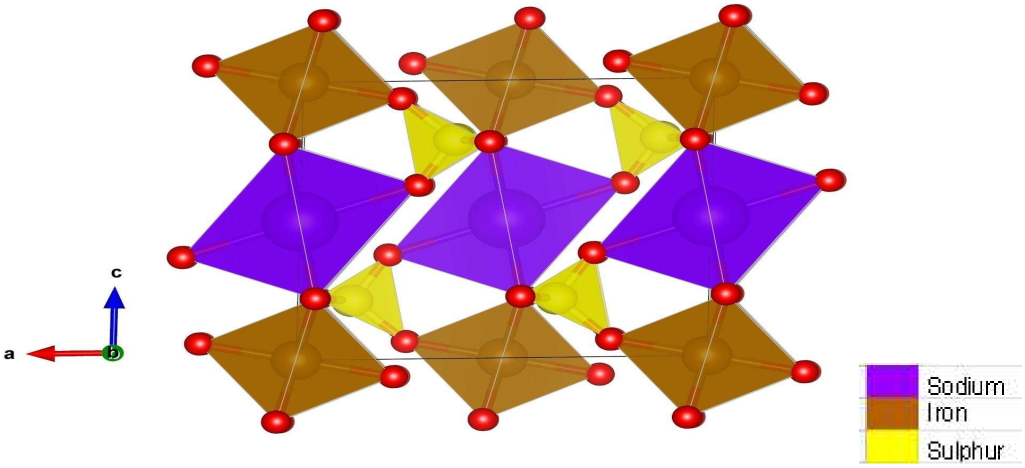

Figure V. Eldfellite crystal structure

Eldfellite crystallizes into an orthorhombic form(Pbca) .

The lattice parameters of yavapaiite crystal structure are a = 8.231 Å b = 5.425 Å, c = 7.176 Å

, and α=90° , β=90°, γ = 90°.

Above figure is a crystal structure of Yavapaiite and the structure presented there is projected into a ac plane.

The purple colour in the crystal structure is sodium and it is at 6 fold coordination.
The brown color in the crystal structure is Iron and it is at 6 fold coordination
The yellow colour in the crystal structure is sulphur, it is at 4 fold coordination
Red ball in the crystal structure represents an oxygen atom.

4. RESULT

Jarosite's data and graphs

To determine the equation of state, we have progressively varied the volume of the unit cell of Jarosite and calculated its total energy using Density Functional Theory(DFT).

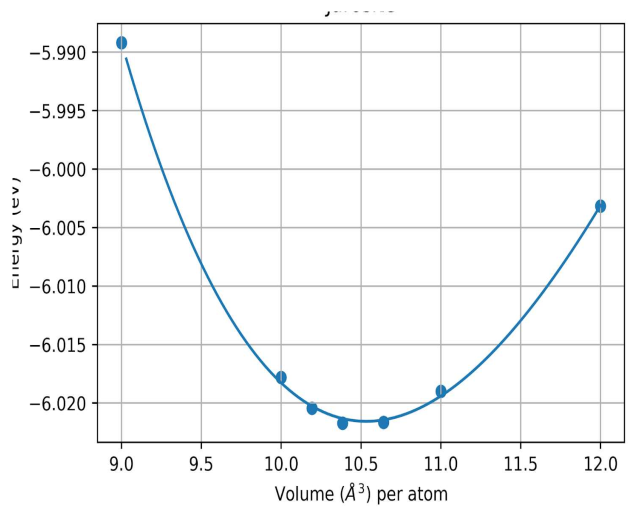

Figure VI . Energy v/s volume per atom plot for Jarosite

This is our calculated Energy v/s volume.We got this data after using DFT. The data set of energy v/s volume is fitted into the 3rd order birch murnaghan equation of state, which yields these fitting parameters.

3rd order of BM fitting parameters
V0 (Å^3)) = 821.5411535
E0 (eV) = -469.6820651
B0 (GPa) = 35.95061444
B0' = 3.965169634

These fitting parameters I got is slightly differ from below experimental fitting parameter:-

Experimental data fitted in 2nd order BM
V0 (Å^3) = 795.1
B0 (GPa) = 55.7
B0' = 4

Using our calculated fitting parameter, we determine the Pressure v/s volume curve for Jarosite as below.

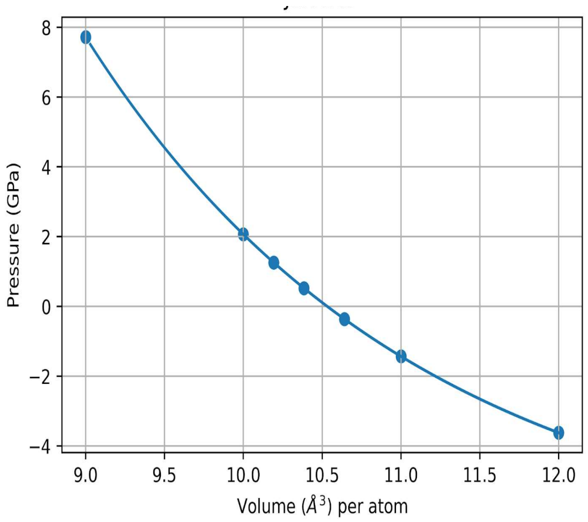

Figure VII . Volume per atom v/s pressure plot for Jarosite

Now , we have pressure and volume , and along the volume we have internal energy. Hence , we can enthalpy and also we can get enthalpy as a function of pressure.

$H = U + PV$

Where, H= Enthalpy, U= Internal energy , P= Pressure and V=volume

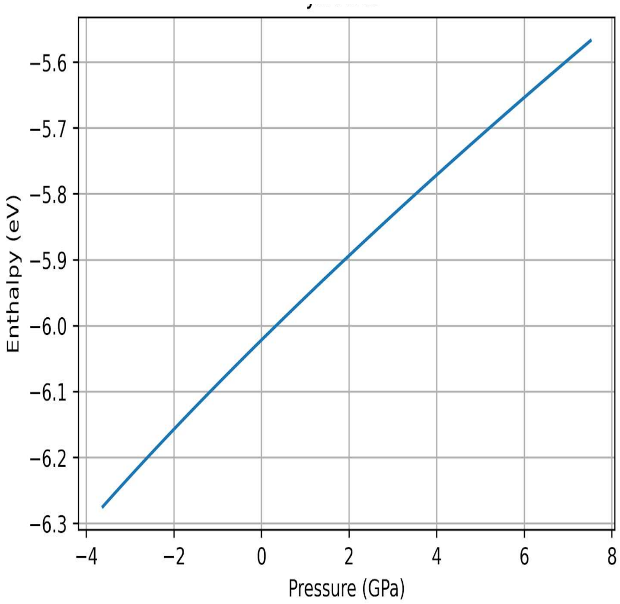

Figure VIII . Pressure v/s Enthalpy($H = U + PV$) plot for Jarosite

Yavapaiite's data and graphs

To determine the equation of state again, we have progressively varied the volume of the unit cell of Yavapaiite and calculated its total energy using Density Functional Theory(DFT), just like we have done for Jarosite.

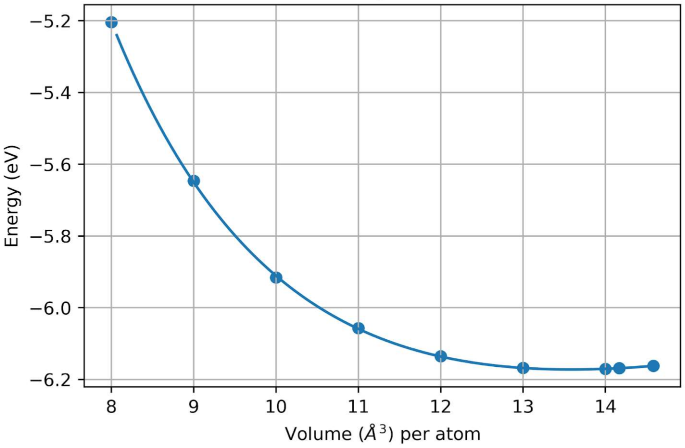

Figure VIII . Volume per atom v/s pressure plot for Yavapaiite

This is our calculated Energy v/s volume.We got this data after using DFT. The data set of energy v/s volume is fitted into the 3rd order birch murnaghan equation of state, which yields these fitting parameters.

3rd order of BM fitting parameters
V0 (Å^3) = 325.9545159
E0 (eV) = -148.1300002
B0 (GPa) = 49.59077349
B0' = 4.682757028

Using our calculated fitting parameter, we determine the Pressure v/s volume curve for yavapaiite.

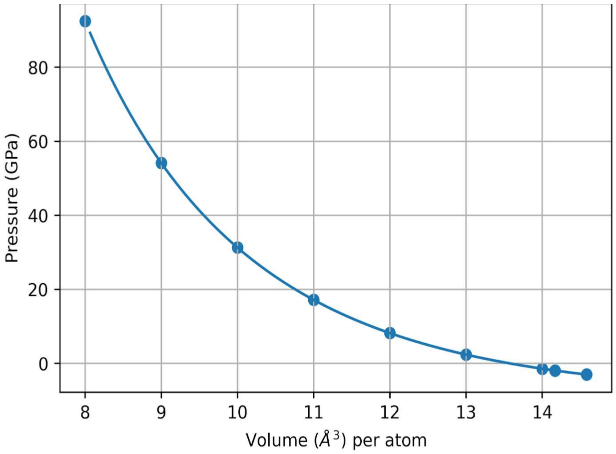

Figure IX . Volume per atom v/s pressure plot for Yavapaiite.

Now , we have pressure and volume , and along the volume we have internal energy. Hence , we can enthalpy and also we can get enthalpy as a function of pressure.

H = U + PV

Where, H= Enthalpy, U= Internal energy , P= Pressure and V=volume

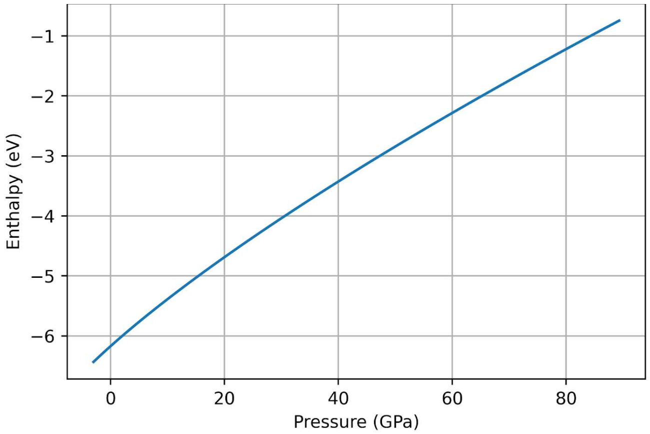

Figure X . Enthalpy(H=U+PV) v/s pressure plot for Yavapaiite

<u>Natrojarosite's data and graphs</u>

Just like we have done for jarosite and yavapaiite, similarly we have done for natrojarosite we got following fitting parameters and graphs.

3rd order of BM fitting parameters	**Experimental data for Natrojarosite**
V0 (Å^3) = 802.4264556	V0 (Å^3) =769.6
E0 (eV) = -459.6478953	B0 (GPa) =50.6 GPa
B0 (GPa) = 53.04326915	B0' =9.9
B0' = 6.061942075	

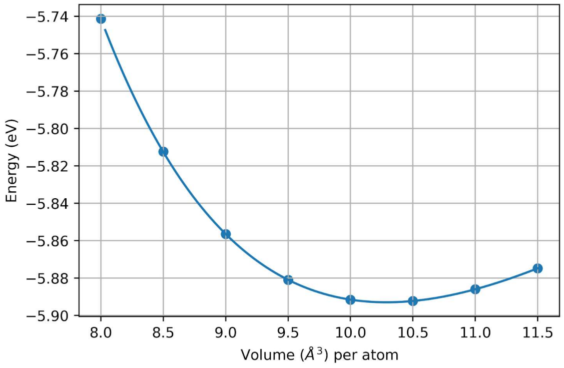

Figure XI . Volume per atom v/s energy plot.

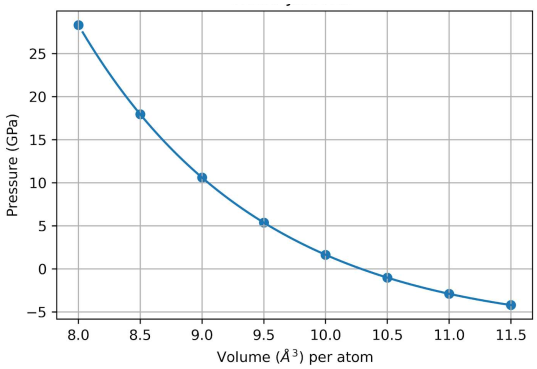

Figure XII . Volume per atom v/s pressure plot.

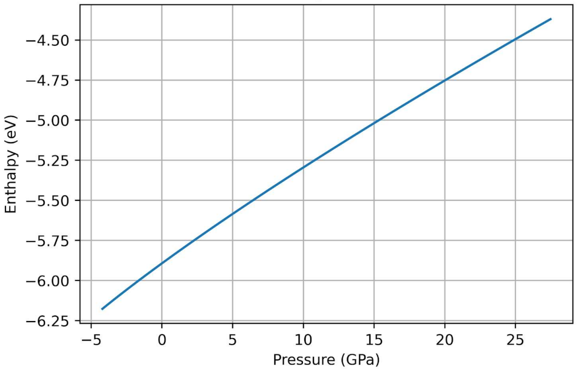

Figure XIII . Pressure v/s Enthalpy(H = U + PV) plot for Yavapaiite.

Eldfellite’s data and graphs

Just like we have done for jarosite, yavapaiite and natrojarosite, similarly we have done for eldfellite we got following fitting parameters and graphs.

3rd order of BM fitting parameters
V0 (Å^3) = 320.3001919
E0 (eV) = -149.6001912
B0 (GPa) = 40.11500889
B0' = 3.595765614

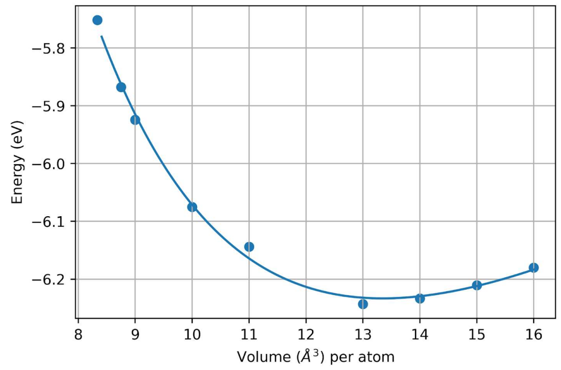

Figure XIV. Volume per atom v/s energy plot.

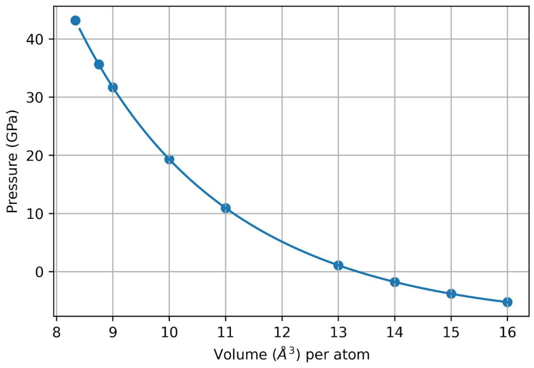

Figure XV. Volume per atom v/s pressure plot.

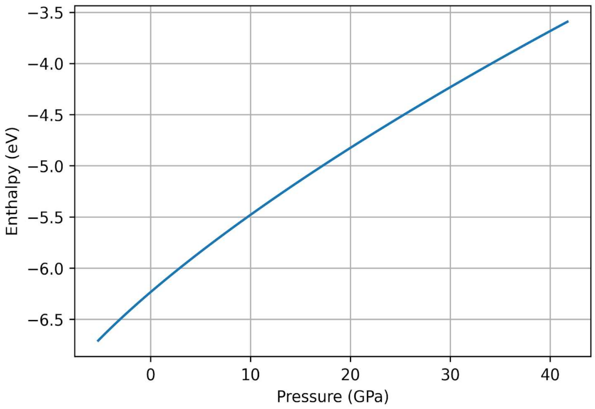

Figure XVI. Pressure v/s Enthalpy(H = U + PV) plot.

5.CONCLUSIONS AND DISCUSSIONS

All calculations have been performed using density functional theories with GGA as exchange correlation functional.

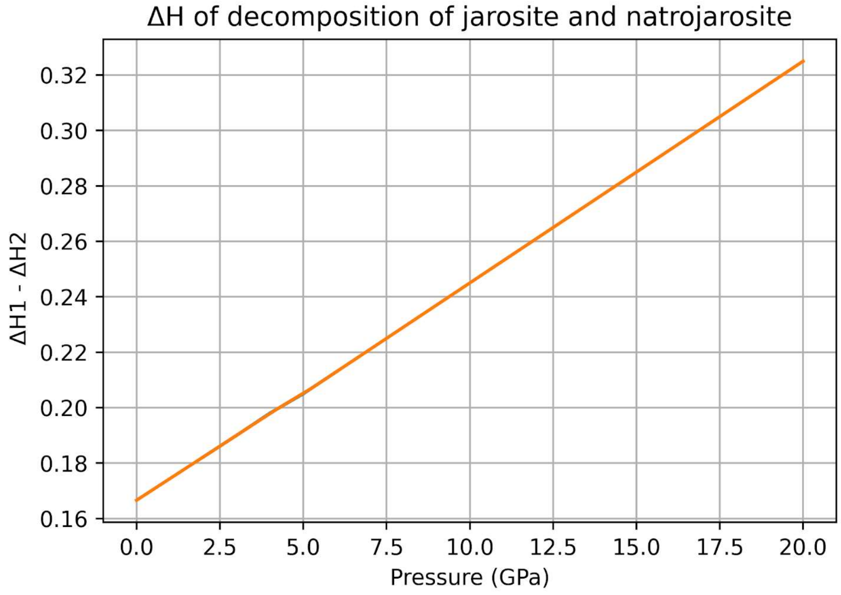

Figure XVII. Pressure v/s ΔH ($\Delta H = \Delta H_1 - \Delta H_2$) plot.

where,

$$\Delta H_1 = \Delta H_{Yavapaiite} + \Delta H_{Hematite} + \Delta H_{Water\ vapours} - \Delta H_{Jarosite}$$

$$\Delta H_2 = \Delta H_{Eldfellite} + \Delta H_{Hematite} + \Delta H_{Water\ vapours} - \Delta H_{Natrojarosite}$$

$$\Delta H = \Delta H_1 - \Delta H_2 = \Delta H_{Natrojarosite} - \Delta H_{Jarosite} + \Delta H_{Yavapaiite} - \Delta H_{Eldfellite}$$

As we can see in this plot, ΔH is increasing as pressure is increasing , this plot indicates natrojarosite is more stable as pressure is increasing. So, we can conclude that in the absence of any temperature effect, Na increases the stability field of Jarosite. This is expected as Na^+(1.02 Å) is smaller than size of that K^+(1.38Å). Therefore, because of smaller size natrojarosite is able to sustain under higher pressure as compared to K-Jarosite and hence Na- Jarosite shows higher stability.

6. FUTURE - WORK

- However, it is important to us to see the effect of the temperature on the reactions which forms a part of the future calculations.
- We should look into the effect of the temperature in the above mentioned reactions.
- This would give us an idea about the condition under which the temperature, Jarosite on Mars would break down and give us water which is important for the sustainability of life on planet Mars.
- Previous calculations show that the pure potassium endmember Jarosite is stable under $18\ ^{o}C$.
- We will look into the effect of sodium substitution at potassium sites on the stability of Jarosite as a function of temperature and pressure in the future endeavours.

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