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H_2O and CO_2 volatiles degassing during Proterozoic igneous activity in Kirana Hills, Punjab, Pakistan

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Abstract

Tecto-magmatic activity had curved the land of the Rodina Supercontinent during the Proterozoic EON. These processes ejected dissolved gases along with other internal material onto the surface. Besides numerous other impacts, atmospheric fugacity is an important aspect of volcanic eruptions, resulting in both long-term and short-term effects on the atmosphere and environment. The present research is an attempt to estimate atmospheric fugacity during igneous activity in Kirana Hills, located in Punjab, Pakistan. H_2O and CO_2 volatile concentration is measured by FTIR at the National Center of Excellence in Geology, University of Peshawar. These results are then calculated with the estimated volume of Kirana Hills to estimate the total atmospheric loading of H_2O and CO_2 during Proterozoic igneous activity. However, Kirana hills have a total volume of about 2642906332.30 cubic meters. It was calculated through x, y, and z values of each pixel of the Digital Elevation Model (DEM). It was then converted into Kilograms, which is 4.61×10^{12} Kg. It was estimated that the prehistoric eruptions at Kirana Hills had released about 1.75×10^7 Kg of H_2O and 4.33×10^7 Kg of CO_2, equal to 1.75×10^4 and 4.33×10^4 tons of H_2O, CO_2, respectively. It is found that the Hachi volcanic group released more gases into the atmosphere than the Taguwali formation. It is also found that the estimated amount of CO_2 is greater than the released amount of CO_2 during the formation of the Deccan traps. Thus, it is concluded that the released amount of greenhouse gas (CO_2) would contribute to climate change by altering atmospheric physical and chemical properties. And climate change would result in drastic environmental changes on this planet.

Keywords: Kirana Hills, Atmospheric Fugacity, Volume of Kirana Hills, Climate Change

Introduction

Volcanic eruptions are the most exalting phenomenon among the dynamic processes of the planet Earth, which exhibit a wide range of variations in their properties determined by the type of volcano, volcanic ejection, and eruption behavior. Different volcanoes erupt different types of volcanic products and behave dramatically (Abbott, 2012; Blij & Muller, 1993; Christopherson, 2012; Hefferan & O'Brien, 2010; Huggett, 2011; Hyndman & Hyndman, 2010; Kirkland, 2010; Lake, 1915; Leakwood & Hazlett, 2010; Mcknight's, 2013; Sigurdsson, 2015; Skinner & Murck, 2011; Strahler, 2011; Tarbuck, Lutgens, & Tasa, 2014). Most often, volcanoes erupt water vapor (H_2O), carbon dioxide (CO_2) and sulfur dioxide (SO_2) abundantly along with other gasses in minor quantity i.e. Hydrogen (H^2), Hydrogen Sulfide (H^2S), Hydrogen chloride (HCl), Hydrogen fluoride (HF), Hydrogen bromine (HBr), Carbon Monoxide (CO), carbon disulfide (CS2), Carbonyl sulfide (COS), Methane (CH4), Boron, Mercury (Hg) Vapor, Organic Compounds, even Gold. For example, in 1996, the Popocatepetl released about 3.9 million tons of SO_2, 16 million tons of CO_2, 0.75 million tons of HCl, 0.075 million tons of HF, 260 tons of As, 2.6 tons of Hg, and roughly 200 million tons of H_2O (Goff et al., 1998). The injection of a bulk of volcanic gases and ash into the atmosphere dramatically alters its physical and chemical properties. For instance, the eruption of Toba volcano on the island of Sumatra in Indonesia dramatically triggered global cooling by injecting a huge amount of SO_2 into the stratosphere. It reacted with atmospheric chemical constituents and formed sulfate aerosol particles and blocking the solar radiation. It is well known largest explosive volcanic eruption of at least the past 100,000 years (Ambrose, 1998, 2003; Haslam et al., 2010; Haslam & Petraglia, 2010; Neudorf, Roberts, & Jacobs, 2014; Oppenheimer, 2002; Robock, 2000; Robock et al., 2009; Rose & Chesner, 1990; Zielinsk et al., 1996). Likewise, some of these catastrophic events are responsible for mass extinctions on this planet. For instance, the formation of Siberian traps accompanied with numerous plausible factors and mechanisms, caused for largest mass extinction at this planet during end of the Permian (250 million years ago). i.e., the huge amount of release of CO_2 and SO_2 aerosol, rapid sea level change, global climate change, acidification of sea water, widespread wild fire, thermo-genic carbon dioxide, and methane, etc. (Kamo et al., 2003; Kiehl & Shields, 2005; Olsen, 1999; Saunders et al., 2005; Shen et al., 2011). The injection of a huge mass of aerosols into the atmosphere triggered a short-term volcanic winter followed by long-term warming. And the sluggish circulation of oceanic water triggered oceanic anoxia. Thus, the evolution of Siberian traps killed more than 90% of marine species and more than 70% of terrestrial species (Erwin, Bowring, & Yugan, 2002; Joachimski et al., 2012; Saunders & Reichow, 2009; Wignall, 2001). Thus, these historic eruptions are evidence that the planet Earth is dramatically affected by volcanic activities. However, volcanic gases are essential products to switch the volcanic eruption style, atmospheric dynamics, and alteration of global climate (Leakwood & Hazlett, 2010). However, the present study is an attempt to estimate the total atmospheric fugacity of H_2O and CO_2 during Proterozoic Tecto-magmatic activity at Kirana hills. This study will help to understand and reconstruct the prehistoric environment.

Material and methods

Study Area

This research was conducted in Kirana Hills, Punjab, Pakistan. Major parts of these hills are located near the towns of Sargodha, Chiniot, Shahkot, and Sangla. The findings of various studies suggest that the Kirana complex is the result of widespread volcanic activity during Proterozoic times, dating back to 750-950 million years ago. A number of researchers donated their lives to explore it (Ahmad, 2000; Ahmad & Chaudhry, 2009; Alam, 1987; Chaudhry et al., 1999; Khan, 2009; Shah, 1977). But, still, there is a lot to discover. Many researchers tried to classify these complexes for more precision of knowledge, i.e. Sharaban Group and Kirana Group (Alam, 1987) Much Super Group and Hachi Volcanic (Chaudhry et al., 1999; Ahmad, 2000). The petrography and mineralogy of dolerites of Hachi Volcanism suggested that these rocks are mainly composed with mafic (dominated by Plagioclase, augite and occasional olivine/ Magnetite) and felsic (dominated by alkali feldspar and quartz. Amphibole and augite are also encountered in basalts/dolerites) tholeiitic basalt rhyolite magma, which is intercalated with mata-sediments. The existence of plagioclase, pyroxene, amphibole, chlorite, epidote, opaque oxide, and calcite indicated that the dolertites suffered from hydro-thermal alteration and low-grade metamorphism under the temperature ranging 1100º °C – 800º C and pressure ranging 5-7 k bar (Ahmad & Chaudhry, 2009; Khan, 2009). It is also a source of some mineralized zones of hematite, copper, gold, silver, and cobalt. Hematite has a higher concentration than other minerals. Silver and gold are found along the dykes in minor amount. But these are not sufficient for commercial purposes (Ahmad & Chaudhry, 2009; Khan, 2009; Shah, 1977). Besides these, some other minerals like sandstone, ordinary sand, and iron have also been discovered. Iron reservoirs are estimated at 109.83 million tons, which was recently explored.

Sample preparation and analysis

Five sample sites were selected as studied by (Khan, 2009; Ahmad & Chaudhry, 2009), and the rock samples were prepared and analyzed at the National Center of Excellence in Geology, Peshawar. The volatiles concentration (wt.%) in rock samples is measured by FTIR from the inert organic compound (0.50g of rock powder and 5 mL methanol, CH_3OH, for each sample). Methanol is an excellent organic solvent and produces water (H_2O) and carbon dioxide (CO_2) by burning in open air (in the presence of oxygen).

$$2\ CH_3OH + 3\ O_2 \rightarrow 2\ CO_2 + 4\ H_2O$$

Volume of Kirana Hills

Top sheet No NH 43-1 series U502 edition 1-AMS (RF = 1:250,000) was used to create a digital elevation model in ArcGIS.

3D Analyst Tool > Raster Interpolation > Topo to Raster

The volume computation deals with pixels' properties (ΔX, ΔY, and ΔZ) and calculates volume in cubic meters (Figure 2).

Equation 1:

$$\text{Total Volume} = \sum (\Delta X * \Delta Y * \Delta Z)$$

The volume of Kirana Hills was then converted into kilograms (1 m^3 = 1746 kg for broken weight trap rocks) (Table 2, 3).

Equation 2:

$$w = \rho \times v$$

Where the Greek letter ρ (rho) stands for density and v is the volume of the object.

Atmospheric Fugacity

The wt.% concentration of volatiles was converted into grams and kilograms (each sample) (Tables 2, 3).

Equation 3:

$$m_{(kg)} = m_{(g)} / 1000$$

The mass *m* in kilograms (kg) is equal to the mass *m* in grams (g) divided by 1000.

The mean weight (Kg) of volatile concentration is further calculated to estimate the total released gas.

Equation 4:

$$M = Mv\ C$$

M is the mass of gas released from the melt in kg. Mv is the mass of magma in kg, and C is the concentration of gas in the melt as a mass fraction (Self et al., 2006)

Results

Volatiles Concentration

The selected samples are divided into two major groups as classified by different researchers (Alam, 1987; Shah, 1977; Chaudhry et al., 1999; Ahmad, 2000). One sample represents the Taugawali formation, and the other three samples represent Hachi volcanic groups (sub-groups include Bulland Hills and check 123). The Hachi volcanic group represents a higher concentration of H_2O and CO_2 volatiles in rock samples than the Taguwali formation group. Hills at Chack number 123 (a subgroup of Hachi Volcanic group) contains the maximum concentration of H_2O, 1.9 wt. % and CO_2 3 wt. %. But the major volcanic group "Hachi" represents a lower concentration of H_2O and CO_2 volatiles than the hill of Chack number 123. It is about 0.8 wt. % H_2O and 1.9 wt. % CO_2. While the Buland hills (a subgroup of the Hachii volcanic group) contain 0.45 wt. % H_2O and 1.85 Wt. % CO_2. These three subgroups are the upper part of the Major Hachi Volcanic group. But the lower part of Hachi volcano contains comparatively low concentrations of H_2O and CO_2 volatiles in rock samples. It is observed that the Chiniot hills contain 0.25 wt. % H_2O and 1.2 w.t % CO_2. It is found that the Hachi volcanic group exhibits a higher concentration of H_2O and CO_2 volatiles than the Taguwali formation group. Only Chiniot hills exhibit lower concentration in both groups "Hachi and Taguwali" (Figure 1). The concentrations of H_2O in rocks of Kirana Hills are very close to the estimated amount of H_2O in MORB, which is estimated by (Sobolev & Chaussidon, 1996). A total of 145 trapped and isolated Mg-rich olivine phenocrysts from basalts and ultramafic lavas have been analyzed for H_2O contents. A general survey was conducted to analyze the distribution of water in primary melts derived from the mantle beneath mid-ocean ridges and above subduction zones. It is found that primate melts of subduction zones basalts have more concentration of H_2O (1.0 and 2.9 wt.% mean at 1.7 wt.%, 84 samples) than mid-oceanic ridges basalt (MORB) (H_2O contents mean at 0.12 wt.% for N-MORB 14 samples, 0.17 wt.% for T-MORB 9 samples, and 0.51 wt.% for E-MORB 14 samples).

On the other hand, the concentration of CO_2 is similar to the recorded concentration of CO_2 during the eruption of Redoubt Volcano, Alaska, in 2009. It is found that the erupted magma contains about 0.9 to 2.1 wt. % of CO_2 (Werner et al., 2013).

Volume calculation

Volume of Kirana Hills

Kirana complex is highly eroded, and it was a daunting task to estimate the appropriate volume. The estimated volume of Kirana Hills is 2642906332.2 cubic meters (Table 1) (Figure 2). The total volume of kirana hills is multiplied by 1746 kg (1 m^3 is equal to 1746 kg) to calculate the total weight of kirana hills. So, the calculated weight of Kirana Hills is 4614514456002.78 Kg.

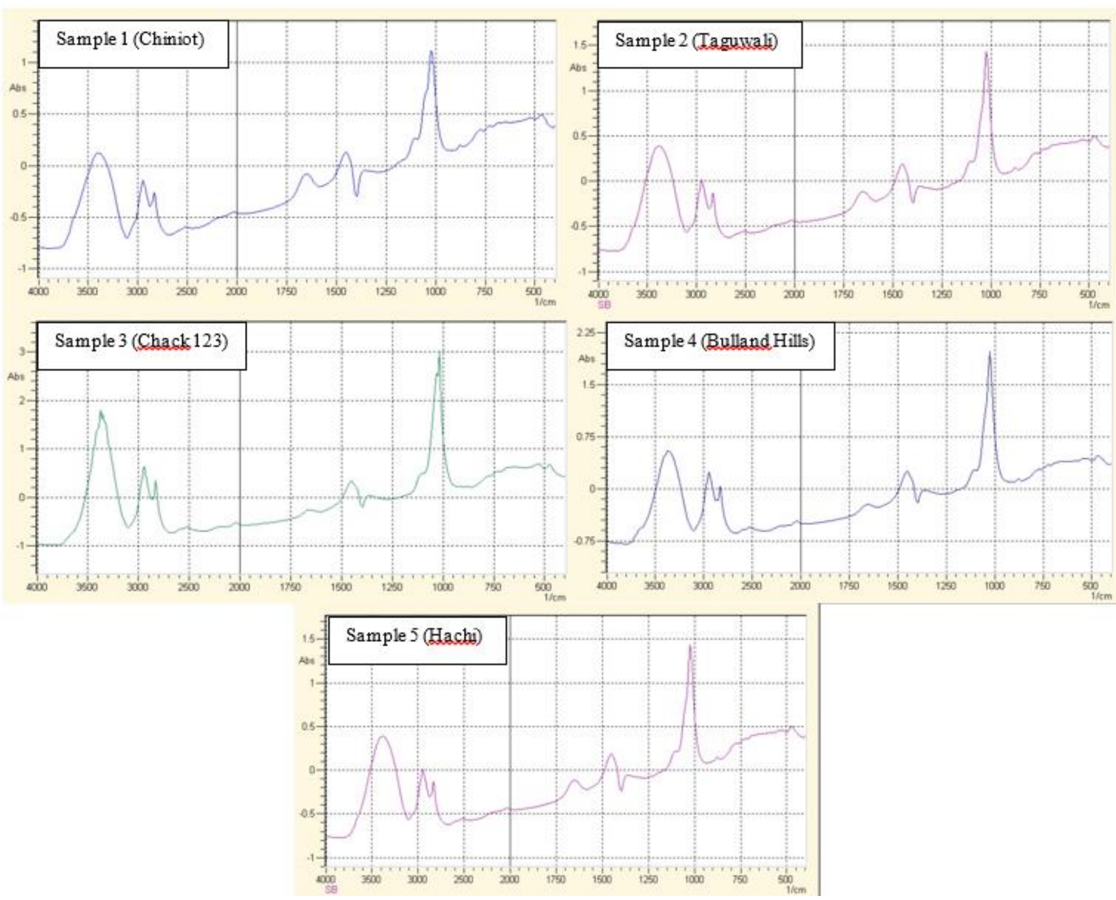

Figure 1. FTIR Absorbance Graphs

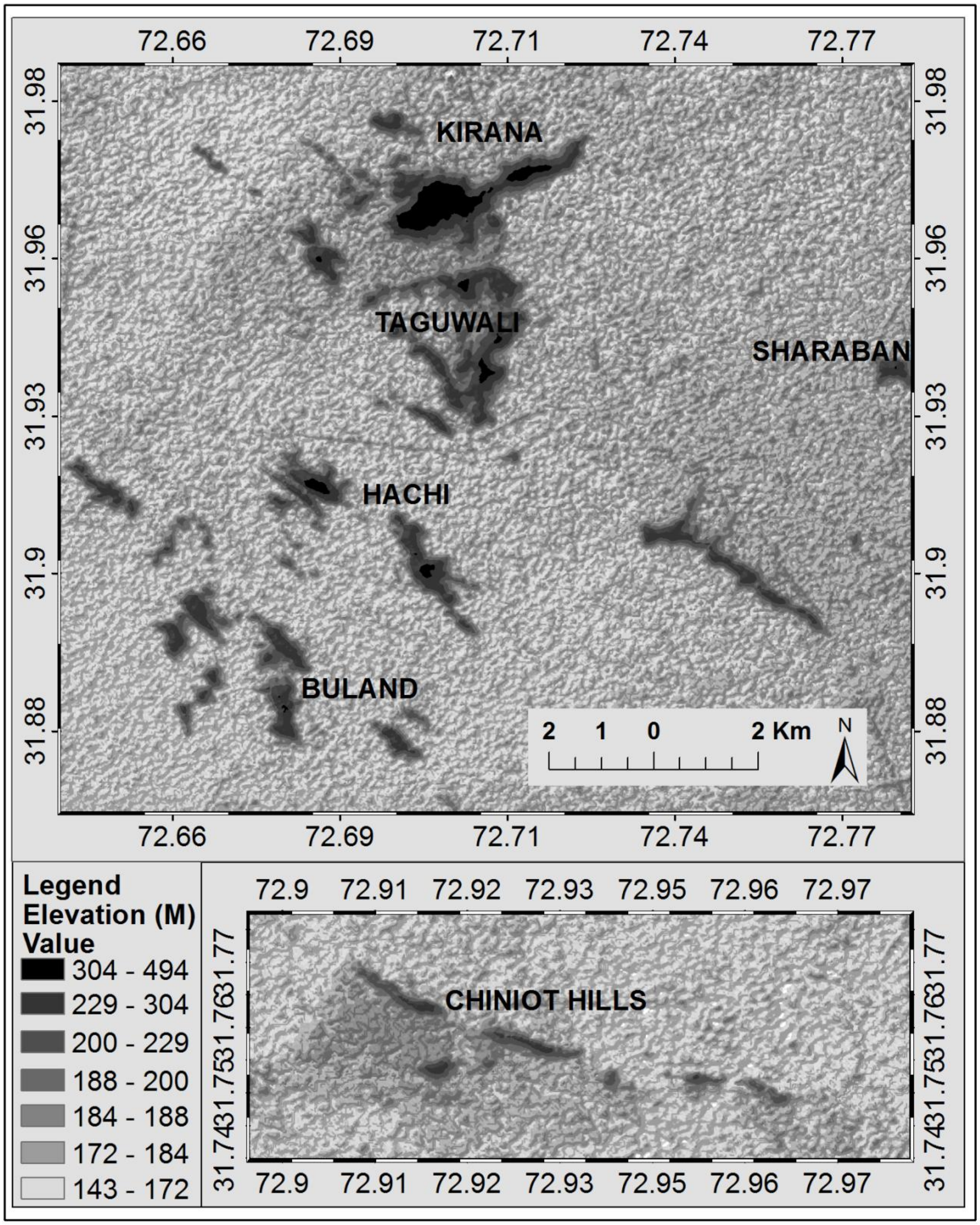

Figure 2. Digital Elevation Model (DEM). Each pixel of the digital elevation model has the value of about (cell size X, Y) 0.0010822675, 0.0010822675.

Table 1. Zonal Statistics of Kirana Hills for Volume calculations, located in Punjab, Pakistan

COUNT	AREA	MIN	MAX	RANGE	MEAN	STD	SUM	Volume
1.0	20453.0	6.2	6.2	0.0	6.2	0.0	6.2	126971.4
8.0	163624.0	-10.7	82.0	92.7	25.7	30.9	205.8	4209716.5
58.0	1186270.0	-17.6	207.7	225.3	68.7	59.7	3986.7	81540560.0
27.0	552230.0	-19.3	161.4	180.7	46.4	44.4	1253.4	25636348.0
12.0	245436.0	-20.1	83.1	103.2	34.5	36.7	413.5	8458040.0
39.0	797666.0	-14.3	278.9	293.2	88.0	76.6	3432.2	70198696.0
8.0	163624.0	-0.2	96.7	97.0	34.0	29.4	272.4	5570457.5
27.0	552230.0	-28.9	131.0	159.8	42.8	41.0	1154.6	23614134.0
80.0	1636240.0	-17.8	228.8	246.6	69.9	63.7	5593.8	114409320.0
7.0	143171.0	-12.2	87.0	99.2	28.4	34.5	198.9	4068999.8
63.0	1288540.0	-19.6	196.7	216.3	70.6	60.2	4450.2	91018720.0
1.0	20453.0	1.2	1.2	0.0	1.2	0.0	1.2	23910.0
18.0	368153.0	-24.1	91.2	115.3	35.4	37.1	636.5	13018641.0
85.0	1738500.0	-18.3	287.4	305.7	98.5	72.9	8371.3	171218432.0
115.0	2352090.0	-18.0	220.0	238.1	60.5	52.0	6957.8	142308512.0
70.0	1431710.0	-20.1	302.9	323.0	109.3	88.8	7648.5	156435328.0
52.0	1063550.0	-18.6	177.5	196.1	77.1	57.3	4007.2	81958928.0
31.0	634042.0	-19.9	295.9	315.8	81.4	79.4	2523.0	51601992.0
57.0	1165820.0	-35.6	192.5	228.1	72.4	61.8	4129.0	84450160.0
4.0	81811.9	11.4	23.3	12.0	15.3	4.7	61.2	1250857.4
217.0	4438290.0	-44.4	331.7	376.1	90.2	80.4	19574.4	400355072.0
92.0	1881670.0	-31.6	289.4	321.0	76.8	73.5	7068.8	144578400.0
48.0	981742.0	-25.1	309.3	334.4	80.1	74.5	3843.0	78600112.0
16.0	327247.0	-14.6	91.5	106.1	23.3	32.4	372.4	7616458.0
1.0	20453.0	-6.9	-6.9	0.0	-6.9	0.0	-6.9	-140974.3
1.0	20453.0	19.0	19.0	0.0	19.0	0.0	19.0	388592.9
1.0	20453.0	34.4	34.4	0.0	34.4	0.0	34.4	703871.1
16.0	327247.0	-13.5	123.0	136.5	33.9	37.9	542.3	11091673.0
234.0	4785990.0	-42.9	461.1	504.0	168.3	126.0	39375.8	805350784.0
37.0	756760.0	-27.4	302.7	330.1	83.6	80.6	3092.2	63243620.0

Zonal statics analysis is applied in ArcMap for the calculation of the volume of Kirana hills at a confidence level of 0.5.

H_2O in Kg

The rocks of Chack number 123 contain the maximum concentration of H_2O content. It accounts for 0.0095 grams (0.0000095 kg) out of 0.5 grams. The sample collected from the major Hachi group contains 0.004 g (0.000004 kg) of H_2O content. On the contrary, Bulland hills contain fewer amounts, 0.00225 g (0.00000225 kg) of H_2O, than Chack number 123 and Hachi group. These three sites are part of the upper Hachi volcanic group. But the lower part of the Hachi volcanic group contains a very small amount of H_2O. It is about 0.00125 g (0.00000125 kg). On the contrary, Taguwali formation contains 0.002 g (0.000002 kg) of H_2O. Though this amount of H_2O is greater than the lower part of the Hachi Volcanic group. Yet, it is the lowest concentration of water content of the whole Hachi Volcanic group (Table 2).

Table 2. Table is representing FTIR results of traped volatile "H_2O" in percentage for each sample (sample weight in grams), and then this percentage is converted in grams and kilograms for further calculation with preciously calculated volume of Kirana hills to estimate the total degassing during the formation of Kirana Hills, located in Punjab, Pakistan.

Sr. #	Sample	Weight-g	H_2O%	H_2O-g	H_2O-kg
1-Chiniot	C2	0.5	0.25	0.00125	0.00000125
2-Taguwali	SB	0.5	0.4	0.002	0.000002
3-Chack 123	C123	0.5	1.9	0.0095	0.0000095
4-Bulland	C128	0.5	0.45	0.00225	0.00000225
5-Hachi	C116	0.5	0.8	0.004	0.000004
				Mean	0.0000038
				M= MV CH_2O	17535154.93

CO_2 in Kg

The results for CO_2 are quite similar to the results for H_2O concentration in different hills' packages of two different rock groups as classified by (Alam, 1987; Chaudhry et al., 1999; Ahmad, 2000). The rocks of Chack number 123 contain the maximum concentration of CO_2. It accounts for 0.015 g (0.000015 kg) out of 0.5 grams. The sample collected from the major Hachi group contains 0.0095 g (0.0000095 kg) of CO_2 content. On the contrary, Bulland hills contain fewer amounts, 0.00925 g (0.00000925 kg) of CO_2, than Chack number 123 and Hachi group. These three sites are part of the upper Hachi volcanic group. But the lower part of the Hachi volcanic group contains a very small amount of CO_2. It is about 0.006 g (0.000006 kg). On the contrary, Taguwali formation contains 0.00725 g (0.00000725 kg) of CO_2. Though this amount of CO_2 is greater than the lower part of the Hachi Volcanic group. Yet, it is the lowest concentration of carbon dioxide of the whole Hachi Volcanic group (Table 3).

Table 3. Table is representing FTIR results of traped volatile "CO_2" in percentage for each sample (sample weight in grams), and then this percentage is converted in grams and kilograms for further

calculation with preciously calculated volume of Kirana hills to estimate the total degassing during the formation of Kirana Hills, located in Punjab, Pakistan.

Sr. #	Sample	Weight-g	CO_2%	CO_2-g	CO_2-kg
1-Chiniot	C2	0.5	1.2	0.006	0.000006
2-Taguwali	SB	0.5	1.45	0.00725	0.00000725
3-Chack 123	C123	0.5	3	0.015	0.000015
4-Bulland Hills	C128	0.5	1.85	0.00925	0.00000925
5-Hachi	C116	0.5	1.9	0.0095	0.0000095
				Mean	0.0000094
				M= MV CCO_2	43376435.89

Estimated Fugacity

The final calculation is based on the previous lab analysis and volume calculation of Kirana Hills. The calculated mean value of H_2O is 0.0000038 Kg. while the mean value of CO_2 is 0.0000094 Kg. The total volume of Kirana Hills is 2642906332.30 m^3, by converting this amount into kilograms, it accounts for 4.61×10^{12} Kg. The mean value of H_2O and CO_2 is multiplied by the estimated volume of Kirana Hills (volume in kilograms). It is estimated that 1.75×10^7 Kg of H_2O and 4.33×10^7 Kg of CO_2 are released during Proterozoic igneous activity in Kirana hills. By converting, the estimated amount of H^2O and CO_2 is 1.75×10^4 and 4.33×10^4 tons, respectively. It is found that the estimated amount of CO_2 is greater than the CO_2 released during the formation of the Deccan traps. Deccan traps released about 1.4×10^{10} kg of CO_2 could be released for every 1 Km^3 of basaltic lava eruption; thus, the total release from an eruption of 1000 Km^3 would be $\sim14\times10^3$ Tg CO_2 (Self, Widdowson, & Jay, 2006). Meanwhile, the emission of CO_2 from the Deccan Traps increased the level of carbon dioxide in the atmosphere. The increased amount of CO_2 was less than 75 ppm, leading to a predicted global warming of less than 1 °C over several hundred thousand years (Caldeira & Rampino, 1990). While our estimates of total release of CO_2 are nearly 3 times greater than the total released CO_2 from the Deccan Traps. It means that the volcanic eruption at Kirana hills drastically altered atmospheric chemistry, leading to more global warming than the global warming caused by the Deccan traps. Similarly, the total amount of H_2O is greater than the released amount of H_2O during the eruption of Baitoushan Volcano in China/North Korea, ca. 969 AD (Horn & Schmincke, 2000). It is considered the largest eruption of the past 2000 years. This eruption also has had a substantial but possibly short-lived effect on the climate.

Discussion

Volcanic eruptions are the most exalting phenomena among the dynamic processes of the planet Earth, which exhibit a wide range of variation in their properties determined by the type of volcano, volcanic ejection, and eruption behavior. These volcanic eruptions have the potential to alter the physical and chemical properties of the atmosphere by injecting immense volcanic gases. There are numerous examples of volcanic eruptions that drastically affected atmosphere and surrounding environment i.e. the eruption of Eyjafjallajökull in 2010, Mt. Pinatubo in 1991, the historic eruption of super volcano Toba 74000 years ago, Formation of Siberian traps 250 million years ago, formation of Deccan blood basalt province 79 AD, eruption of Mt Vesuvius and so on. Thus, the study of atmospheric fugacity is very crucial to understanding the dynamic processes of this planet. In connection with this, the Kirana complex is investigated to estimate the total historic atmospheric fugacity. The results suggested that these rocks are richer in carbon dioxide (CO_2) than in water (H_2O) content. The rocks at Chack number 123, Bulandhails, and Hachi volcanic group exhibit higher concentration of carbon CO_2 and water H_2O content compared to the Taguwali formation group and Chiniot hills. Hence, the manipulation of these results and mathematical calculations revealed that CO_2 is injected in greater amounts than H_2O into the atmosphere during Proterozoic igneous activity in the Kirana complex. It is concluded that the estimated amount of CO_2 is greater than the CO_2 released during the formation of the Deccan traps. Whereas, Deccan traps released about 1.4×10^{10} kg of CO_2 could be released for every 1 Km^3 of basaltic lava eruption, thus the total release from an eruption of 1000 Km^3 would be $\sim14\times10^3$ Tg CO_2 (Self, Widdowson, & Jay, 2006). Thus, the emission of CO_2 from the Deccan traps increased the amount of carbon dioxide in the atmosphere. The increased amount of CO_2 was less than 75 ppm, leading to a predicted global warming of less than 1 °C over several hundred thousand years (Caldeira & Rampino, 1990). While our estimates of total release of CO_2 are nearly 3 times greater than the total released CO_2 from the Deccan Traps. It means that the volcanic eruption at Kirana hills drastically altered atmospheric chemistry, leading to more global warming than the global warming caused by the Deccan traps. The effects of this research would be very prolific for the reconstruction of the prehistoric environment. It will also be helpful to understand prehistoric atmospheric chemistry and its effects on the environment. It will also be very useful in understanding the prehistoric geological settings of this region.

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