Geochemistry and global cycle of silicon as energy carrier for the development of renewable energy from biomass

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Abstract: Fossil energy Reserves are diminishing and total energy demands however are intensely growing. Their unsustainable nature from the point of view of future availability and environmental impact, has spurred an interest in diversification of energy sources, with particular interest in renewable energy. The solar energy industry is a player in the renewable energy segment, and the electricity generation from solar cells is considered one of the key technologies of the future. Silicon has a very broad spectrum of usage nowadays and it lies at the heart of much modern solar energy technology. Rice is one of the major crops grown through the world. Due to its high silicon content, rice husk (RH) has become a source for preparation of elementary silicon. Si is one of the most widely used resources in modern technology. Despite the fact that Si is the second most abundant element in the earth's crust, processes to form Silicon is usually complex, costly and energy intensive. Development of a simple low energy and sustainable production of Si from RH as biomass is desirable and welcome by many industrial applications. This study highlights the renewability of Si and shows a dry and wet chemistry way to determine it from RH combining a microwave heating method and acid digestion.
Keywords: Energy, rice husk, silica, silicon, photovoltaic.

Introduction

Wide-reaching concerns over energy related climate change combined with spiraling cost of fossil fuels has increased interests in renewable energy alternatives. Although solar photovoltaic power generation is a proven technology, development of this technology to meet terrestrial energy demands has been limited. One of the issues that have limited the widespread use of solar photovoltaic power has been the high cost associated with the materials used in fabricating the solar cells.

Silicon is the second most abundant element in the earth's crust, second only to oxygen. In the Earth's crust, it occurs in thesoil solution at $0.1– 0.6$ molm^{-3} as Si(OH)4; [1]. The dry matter of some plants contains very variable amounts of the element: 1.3–47.3 mg per gof plant dry matter.

Silicon is naturally found as fairly pure silicon dioxide and as silicates. The silicon dioxide is found as huge deposits of quartzite or quartz sand. Three major applications have since greatly stimulated the production and purification of silicon, that is, as an alloy in aluminum, silicones and solid-state electronics. Over the past years, the photovoltaic industry has been experiencing a strong economic growth world-wide. This expansion is due to an increasing demand for PV modules which is expected to continue in the coming years.Currently silicon is the dominant semiconductor material used in the fabrication of most commercially available solar cells or modules, commanding over 90% of the market share of all PV technologies [2].Photovoltaic solar electricity presents an elegant means for electricity generation, as there are no moving parts, zero emissions, and no noise.

Bulk Silicon is usually produced for industrial applications by the carbothermic reduction of silicon dioxide in submerged-arc electric furnace. The process is energy intensive requiring temperatures greater than 2000°C, which are well above the melting point of silicon (1410°C) [3]. Solar-grade Si from RH was obtained by carbothermic reduction; the energy input was reduced to 50 kWh/kg from 200 kWh/kg in the Siemens process. Alumino-thermic reduction should require even less energy due to the considerably lower temperature of reduction. Further reduction of Al content is required by slagging or directional solidification[4].

Since the major sustainability and security challenges we face arise primarily from energy use, biomass processing is taking a significant impact on energy production and utilization.

Electricity generated from silicon can be considered as renewable only if the power utilized in silicon production is derived from renewable sources, with the silicon production process itself also needing to be carbon-neutral. It is left a subject to ascertain which carbon-neutral silicon technology might be best suited to large scale silicon production. *Auner and Holl*suggest a process based on reacting silica with hydrofluoric acid[5].

I. Renewability of biomass and energy

Energy carrier from biomass is hypothetically promising option since this is derived from renewable source, it has a closed carbon cycle and do not contribute much to the greenhouse effect. The importance of biomass with regard to energy production lies on its renewability. Biomass and energy can be replenished in a short period of time due to the cyclic nature of the processes leading to their synthesis through combination of biogenic elements. The cycle of the elements is the combination of many different physical, chemical, and biological processes that transfer them between the major storage pools: the atmosphere, plants, soils, freshwater systems, oceans, and geological sediments. It is a set of phenomena that assure the continuous flow of single mineral elements in the form of ions to more complex organic substances and inversely the return of the organic state in the mineral state. The transport of substances in biogeochemical systems can be represented graphically by means of flowcharts, which are composed of boxes connected by arrow-directed lines.(Fig. I)[6].The symbol M (with units of mass or moles) stands for matter; Ma matter in atmosphere; Mt in earth; Mo; that in oceans; Md matter in deep oceans; F (the exchange rates or flows F's have units of mass or moles per unit of time) stands for flux; Fta: flux from earth to atmosphere; Fat: that of atmosphere to earth; Foa: flux from ocean to atmosphere; and Fao: that of atmosphere to oceans. A quantitative description would give numerical values of the amounts and fluxes for the F's in terms of the M's.
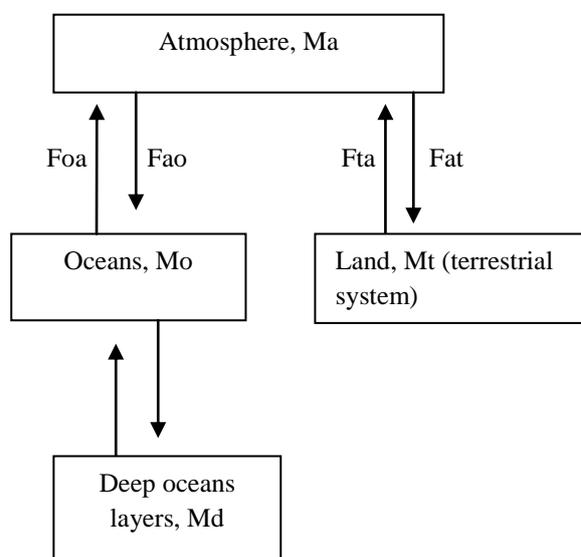

Fig.I [6]: Schema of pools representation of global carbon cycle

Carbon (C) and silicon (Si) cycles are important factors in the regulation of atmospheric CO2 concentrations and hence climate change. Theoretically, these elements are linked by chemical weathering. Chemical weathering of silicate minerals consumes atmospheric CO2 and stoichiometrically produces dissolved silica (DSi, referred to silicic acid, H4SiO4) and HCO_3^-[7].

These solutes are transported to the coastal zone and lakes by rivers where the carbon can be synthesized into organic matter by phytoplankton and the silica can be used to produce diatom frustules. Ultimately, some of these organisms sink to the bottom sediments where carbon (C) and silicon (Si) can be sequestered. Thus, silicate weathering has a net-sink effect on atmospheric CO2 [8]. However, this is not the case for carbonate mineral weathering by carbonic acid, because CO2 is re-released to the atmosphere when carbonate mineral is re-precipitated on geological time scales (>10 to 100 ka). Besides, strong acids (i.e. sulfuric and nitric acid) from anthropogenic sources have enhanced carbonate weathering and CO2 evasion[9].

I.1. Silicon Cycle

With regard to the biogeochemical cycle of Silicon, the Earth's surface environment is divided into four compartments (Fig.2.) [10]: continents, proximal and distal, coastal zones, and the open ocean. These compartments are linked to one another via the water cycle. The fluxes of reactive silica include the sources and sinks of reactive Si for the Earth's surface environment (Figure 2). The sources are chemical weathering on land and flux of *dissolved* Si, *DSi* to the oceans resulting from basalt-seawater interactions. The sinks are burial of bSiO2 in sediments and removal of DSi due to reverse weathering reactions in shelf sediments [11].

A global mass balance of the biologically active part of the Si cycle is derived on the basis of a systematic of existing data regarding terrestrial and oceanic production fluxes, reservoir sizes, and residence times for DSi and bSiO2.
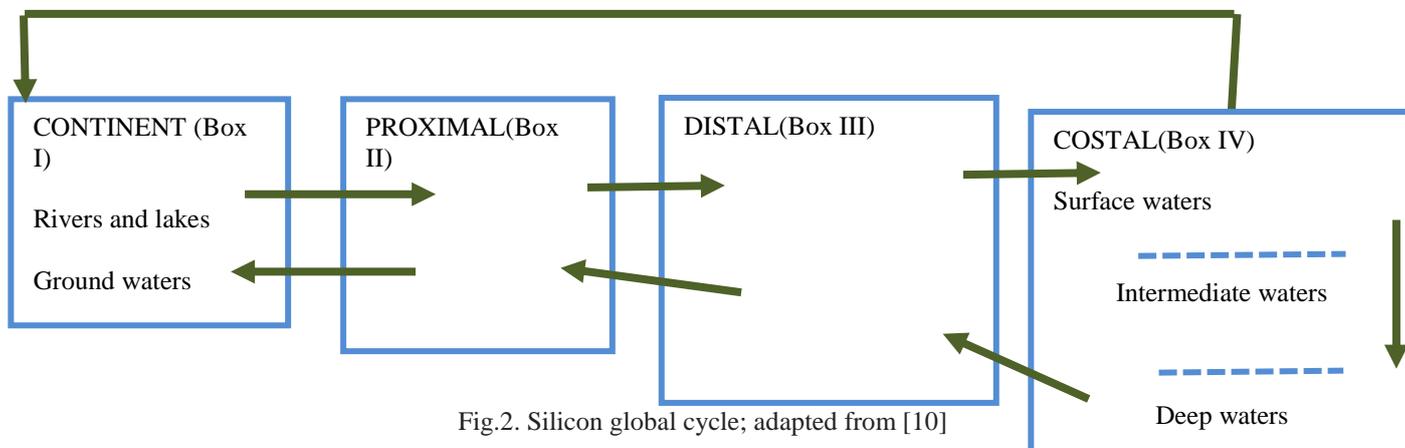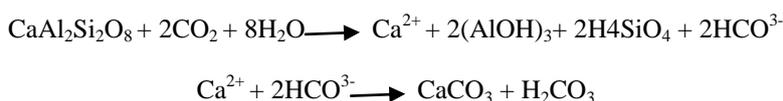

Fig.2. Silicon global cycle; adapted from [10]

The leading transformation processes in the overall biogeochemical Si cycle are uptake of DSi followed by biomineralization as bSiO2 in terrestrial plants and aquatic organisms, and the dissolution of bSiO2 into DSi.DSimainlyconsists of undissociated monomeric silicic acid, Si(OH)4,and represents the main form under which silicon can beassimilated by organisms.Organisms use DSi to build structural elements made ofamorphous, hydrated silica, part of which is preserved afterthe death of the organisms [12]. Here, bSiO2 includes theamorphous silica in both living biomass and biogenicdetritus in open waters, soils and sediments. It should benoted that bSiO2 may undergo significant chemical andmineralogical changes [13].

On land, large quantities of DSi are fixed by higher plantssuch as rice,barley, and deposited as amorphous silica in so-called phytoliths.Silicon in soil and earth's crust is important both in inorganic and biogeological processes. Silicate mineral weathering is to a large extent driven by CO2 consumption. This process initiates the transformation from solid silicate to solute dissolved Si (DSi) in the soil water and is ready for uptake by land plants into a biogenic Si (BSi) form of phytolith.

The silicate weathering process consumes CO2. For example, in the weathering of anorthite (over kaolinite) to gibbsite, DSi is produced and CO2 is consumed [3]:

$$CaAl_2Si_2O_8 + 2CO_2 + 8H_2O \longrightarrow Ca^{2+} + 2(AlOH)_3 + 2H4SiO_4 + 2HCO^{3-}$$

$$Ca^{2+} + 2HCO^{3-} \longrightarrow CaCO_3 + H_2CO_3$$

On the other hand, DSi is transported to the ocean via riverine delivery which is largely controlled by biocycling of freshwater diatom or abiotic dissolution/precipitation of suspended matter. Si is essential nutrient for many forms of marine organisms, such as diatoms, sponge spicules, silicoflagellates, and radiolarians. These organisms account for most of the Si cycling in the ocean, especially diatoms which constitutes 95% of primary production.

Silicon (Si), in the form of dissolved silicate (DSi), is a key nutrient in marine and continental ecosystems. DSi is taken up by organisms to produce structural elements (e.g. husk, hulls and phytoliths) composed of amorphous biogenic silica (bSiO2). Silicon is translocated from the roots as silicic acid through the xylem until it deposits under the cuticle and in intercellular spaces [14].Silicon is absorbed by the plant as monosilicic acid, the absorbed water is lost through transpiration and the silicon stays in the plant tissue when silicon concentration increases in the plant, monosilicic acid polymerize into silica gel through a non-enzymatic reaction [15].The chemical nature of polymerized silicon has been identified as Silica gel. Of the polymerized silica within the plant, 87-89% exists as a very slightly soluble form in hulls, leaf blades, and leaf sheaths. [16].Sangster *et al*. (2001) studied that after 8-10 days of silica gel formation, silicon was almost exclusively found in a solid form in the aerial parts. 11.

Thus amorphous silica is virtually the only form of silicon in plants. Amorphous silica particles that precipitate in plant cells are called Phytoliths or Plant opal. Phytoliths can be assembled without any energy by polymerization of silicic acid when its concentration exceeds 2 mM. Proportions and locations of phytoliths vary with the species, but also with the age of the plant.

The availability of dissolved silicate can dramatically affect the structure, health and productivity of marine, freshwater and terrestrial ecosystems[17]. Some organisms have an absolute requirement for silicon. For instance several plants belonging to *graminae* family, namely, rice, wheat, barley, are the main sources of biogenic dissolved monosilicic acid, Si(OH)4.These organisms use dissolved silicate to build structural elements of hydrated, amorphous silica, or biogenic opal. The overall reaction describing this biomineralization process is as follows.
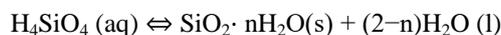
$$H_4SiO_4 \text{ (aq)} \Leftrightarrow SiO_2 \cdot nH_2O\text{(s)} + (2-n)H_2O \text{ (l)}$$

It has been formal that silica is highly concentrated in the inner and outermost surfaces of the epidermal twice. As a result, rice husks are relatively friable, brittle and abrasive. The term white ash refers to residue obtained from complete combustion of rice husk; it is chiefly composed of silica (86-97%). Silica occurs in nature mainly in three crystalline foms namely quartz (hexagonal), cristobolite (white) and tridymite (hexagonal); also in amorphous form like opal and silica in rice husk being essentially of amorphous nature. But it can be connected into any of above three crystalline forms by heat treatment at different temperature

The productivity of the main group of primary producers in the oceans, diatoms, isdirectly dependent on the supply of dissolved silicic acid. For normal growth, diatoms need about as much silicon as nitrogen (on a molar basis). When nutrients are plenty, diatoms can displace other primary producers, because of their relatively high photosynthetic capacity and low maintenance energy requirements.

To summarize the discussion so far, the following, admittedly simplified, outline ofthe biogeochemical cycles of the major elements involved in biomineralization can bedrawn. The continents are the main site of mobilization of C, Si, P and Ca from thelithosphere. The elements typically remain on land for a few thousands of years, duringwhich they participate in the biogeochemical cycles of terrestrial and aquatic ecosystems[13].They are then delivered to the oceans, where they reside for periods ranging from 10^4 to10^6 years. After extensive recycling within the ocean-atmosphere system, they areultimately removed by burial in sediments. Tectonic processes close the cycles by returningthe elements to the earth surface, on time scales of tens to hundreds of millions of years.

I.2. Silica in rice husk

Terrestrial plants play a major role in the evolution of landscapes and in global geochemical cycles. Roots and associated microorganisms produce organic acids and chelates, which enhance the chemical weathering of soil minerals and the release of elements in soil solutions[18].Enhanced chemical weathering provides pools of elements, which are taken up, stored and recycled at various rates by plants, and are ultimately released in streams at a rate up to 18 times the rate calculated for bare watershed.

Although silicon is not essential to plants, it is considered beneficial because it alleviates both biotic and abiotic stresses. Plants take up Si from the soil solution as silicic acid, which, after translocation to the shoots, is polymerised through water evaporation and precipitated as phytoliths.Silicon is considered a beneficial element for higher plants [19],it is fundamental for rice production. Silicon absorption by plants occurs as monosilicic acid (H4SiO4), being proportional to the Si concentration in soil solution for monocotyledons. It behaves as a very weak acid, and even in pH 7.0, only 2 mg kg-1 are ionized (H3SiO4-); as pH increases the degree of ionization increases. Monosilicic acid concentration in soil solution is variable, from 1 to 100 mg dm-3 SiO2[20].

Several plants belonging to *graminae* family, namely, rice, wheat, barley, are the main sources of biogenic dissolved monosilicic acid, Si(OH)4 (4,6). It has been formal that silica is highly concentrated in the inner and outermost surfaces of the epidermal twice. As a result, rice husks are relatively friable, brittle and abrasive. The term white ash refers to residue obtained from complete combustion of rice husk; it is chiefly composed of silica (86-97%). Silica occurs in nature mainly in three crystalline foms namely quartz (hexagonal), cristobolite (white) and tridymite (hexagonal); also in amorphous form like opal and silica in rice husk being essentially of amorphous nature. But it can be connected into any of above three crystalline forms by heat treatment at different temperature

The major constituents of rice husk are cellulose, lignin and silica. During growth, rice plants absorb silica and other minerals from the soil and accumulate it into their structures. Its composition varies with the diversity, climate and geographic location of growth. The high grade of silica in the husk opens a possibility for its valorization. Through thermal treatment by calcination, with or without energy recovery, the ash obtained is constituted by amorphous silica with high porosity having potential application as ligand in construction materials, catalyst support, metals adsorbent, insulation or ceramics, among others.

II. Materials and methods

RH was collected from several locations; an average sample was burned out at 700°C in a muffle furnace for 6 h to produce and investigate RHA SiO_2 with SEM, XRD. The obtained RHA was characterized in terms microstructure by XRD (PHILIPS with Cu Kαradiation) and SEM (JEOL, JSM-5800 LV). Si from RH was extracted by following ways and means:

1) Microwaves ashing coupled with HNO3 leaching: RH is weight into silica glass vessels and HNO3 (Merck, Germany) is added. The samples were put into a microwave-heated pressure digestion system (Ultra Clave II; MLS GmbH, Germany). They were digested and left to cool down to room temperature. Then the digests were transferred to 10-ml volumetric flasks and filled up to the mark with ultra-pure water [21].

2) Microwaves ashing coupled with HNO3+HF leaching: RH is weight into silica glass vessels and HNO3 (Merck, Germany) is added. The samples were put into a microwave-heated pressure digestion system (Ultra Clave II; MLS GmbH, Germany). They were digested, after digestion 0,5 ml hydrofluoric acid was added and left to cool down to room temperature. Then the digests were transferred to 10-ml volumetric flasks and filled up to the mark with ultra-pure water.

3) Melting digestion: RH was glowed for 3 hours at 450°C in platinum crucibles. A mixture of 0.2 g Di-Lithiumtetraborat and 0.8 g Lithiummetaborat is added. The blend were mixed with a plastic spatula and melted at 1100°C for about 30 minutes. The Melts were transferred in a beaker with HNO3 and heated up to the melt is completely solved. Then the sample is filled up to a volume of 250 ml with ultra-pure water. Si content was measured ICP-OES against an external calibration by means of Vista Pro, Varian, Australia equipped with a Scott type spray chamber, a Meinhard type nebulizer and operated at a plasma power of 1.1 kW.

Results and discussion

The RHA sample after burning out at 700°C for 4 h presented a high amount of silica (Fig. 1). The relative contents of other elements increased in general with increase in temperature and time. The crystalline, amorphous or both silica forms depend on the burning temperature or the method used for ash production[22]. When the burning temperature of RH is high, the silica contained in the ash is predominantly crystalline.

Inorganic content of RHA has a high amount of silica (95.33 %). The silica presented is not completely in the amorphous form since its diffractogram showed a sharp 2θ angle diffraction peak centered at 22, which indicates a crystalline structure. The major reflections or peaks of crystalline quartz occur at 2θ angles of 36.541°. It can be seen that no defined peaks corresponding to these 2θ angles are found in Figure. A rather broad peak spanning 2θ which is characteristic of amorphous structures is observed.
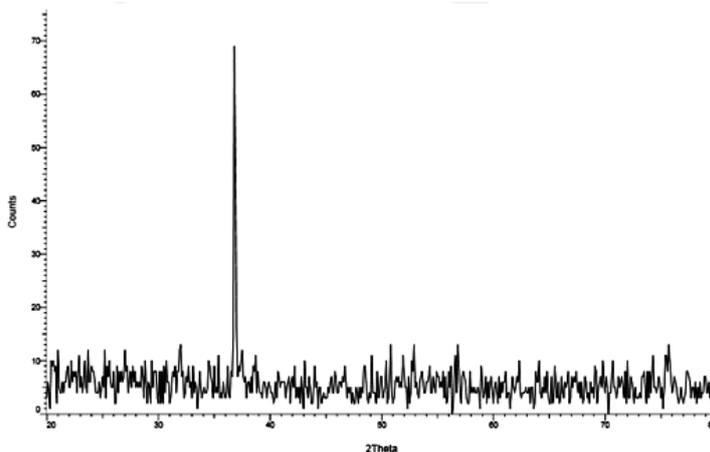

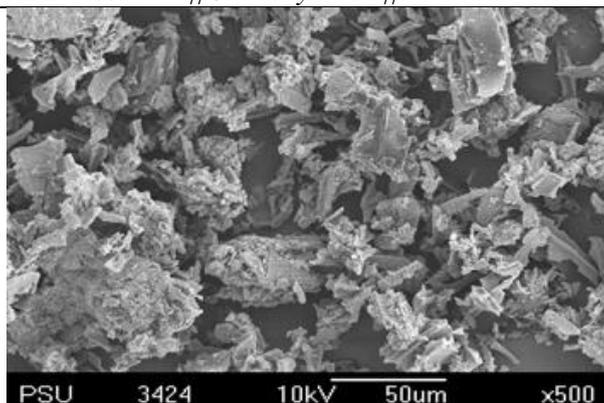Fig.1: X-ray diffraction pattern of silica produced from RHA.

Fig.2: SEM pattern of silica produced from RHA.

SEM shows a porous and multifaceted particle shape and size. The micrograph shows a porous and multifaceted particle shape and size. The amorphous hump after the thermal treatment shows that the RHA is composed mostly of amorphous silica, but still contains quartz as crystalline form of SiO2. The foremost constituents of rice husk comprise hydrated silica, cellulose and hemi cellulose component totaling a 55-60% and lignin component of approximately 22%. The porous and honeycomb morphology seen can be credited to the burning out of the organic component in the rice husk during combustion. The hydrated silica afterward polymerizes to form a skeletal silica network which may explain the flaky and honey comb-like structure.

Table1 shows the experimental results of Si extraction. They indicate that the most efficient method represents the melting digestion followed by microwave ashing with HNO3+HF leaching.

Table 1: Silicon extracted from RH from different localities (mg/kg)

RH-origin	Si (mg/kg) Microwave(HNO3)	Si (mg/kg) Microwave (HNO3+HF)	Si (mg/kg) Melting digestion
Beyla	1,110	58,343	69.012
Boké	1,011	56,007	66,543
Coyah	1,031	54,310	68,121
Dabola	0,935	57,210	67,340
Dinguiraye	1,014	58,481	68,491
Dubréka	0,975	52,893	56,789
Faranah	1,002	56,121	64,231
Kerouane	1,012	55,323	63,470
Kissidougou	1,122	59,011	65,094
Kouroussa	1,011	58,232	68,334
Mamou	1,007	55,112	66,121
Mandiana	1,111	57,223	66,332
Siguiri	1,001	57,001	67,121
Télimélé	1,009	54,200	66,122
Tougué	1,434	55,009	67,210

The microwave ashing combined with HNO3 treatment seems to be the less efficient; the amount of Si extracted by this method does not exceed 1,2 mg/kg Si, independently of RH-origin. Nitric acid is a strong oxidant and tends to provide oxygen to Si extracted by the microwave heat treatment. In average the Si quantity obtained by microwave combined with HNO3 represents 1,80% and 0,532 % of the same generated by the microwave ashing combined with HNO3+HF mixture and the melting digestion respectively. Melting digestion produces more silicon than the other two methods; but it requires much more energy.

The HF contributes much in the extraction. It is well known that Si is thermodynamically unstable in air or water; it reacts spontaneously to form an oxide film. The oxide can be nonstoichiometric and hydrated to various degrees, though the simple empirical formula is silicon dioxide, SiO_2. Silica is a key thermodynamic sink in the silicon system. SiO_2 is an electrical insulator that forms passivating films on crystalline silicon; preparation of porous silicon thus requires an additive in the solution to dissolve the oxide and allow electrochemical oxidation to continue [23].

The Si–F bond is the only bond stronger than Si–O, and it is the Si–F bond enthalpy that drives the main chemical dissolution reaction used to make porous silicon. In the presence of aqueous HF, SiO_2 spontaneously dissolves as SiF_6^{2-} as shows the equation:

$$SiO_2 + 6\ HF \rightarrow SiF^{2+}_6 + 2H^+ + 2H_2O$$

The reaction of SiO_2 with HF is a habitual industrial reaction. It is used to make frosted glass from plate glass and to remove SiO_2 masking layers in the processing of silicon wafers in microelectronics. The silicon hexafluoride ion (SiF^{2+}_6) is a stable dianion that is highly soluble in water. Thus fluoride is the most important additive used in the preparation of silicon, dissolving the insulating oxide that would otherwise shut down the electrochemical corrosion reaction.
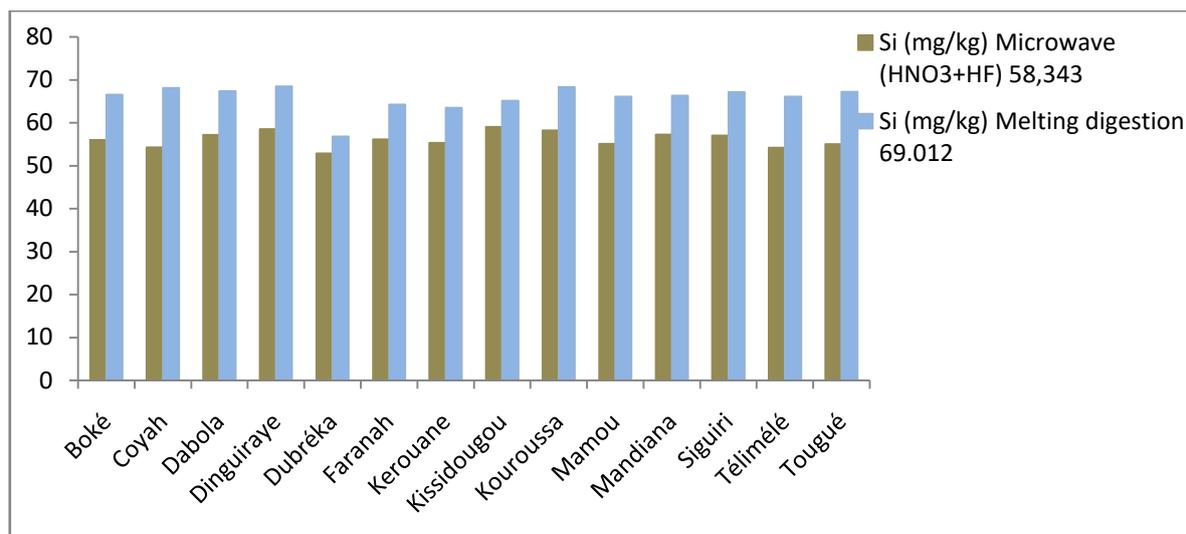

Fig.3 shows that the amount of Si extracted by microwave ashing coupled with HNO3+HF leaching and that obtained by the melting digestion are closed. The origin of RH has no influence on the Si extraction rate.

Conclusion

As carbon-based primary energy carriers become increasingly exhausted, the search for and development of alternative energy sources are of eminent importance. A possible approach to this problem is the employment of so-called renewable energy. Silicon compounds have found prospective application in a number of industrial fields but sustainable, cost-effective, and scalable synthesis of them from sustainable sources still remained challenging. Silicon extracting from RH becomes a crucial technology for its comprehensive utilization of waste. The proposed process is energy effective; it is a useful technique for waste disposal and utilization. In this study the melting digestion of Si is the most efficient method followed by microwave ashing combined with HNO3+HFdigestion.

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