Volcanic Contributions to the Global Carbon Cycle

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Volcanic Contributions to the Global Carbon Cycle

Vicky Hards

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British Geological Survey offices

Keyworth, Nottingham NG12 5GG

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Geological Survey of Northern Ireland, 20 College Gardens, Belfast BT9 6BS

☎ 028-9066 6595   Fax 028-9066 2835

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☎ 01491-838800   Fax 01491-692345

Columbus House, Greenmeadow Springs, Tongwynlais, Cardiff, CF15 7NE
☎ 0 2920 521962   Fax: 02920 521963
email: bgswales@bgs.ac.uk

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU

☎ 01793-411500   Fax 01793-411501
www.nerc.ac.uk

Foreword

In order to address the global warming threat posed by anthropogenic greenhouse gases, many countries have committed themselves, through the recently ratified Kyoto Protocol, to a reduction in their greenhouse gas emissions from 1990 levels during the period 2008–2012. This report presents part of a study commissioned by the International Energy Agency (IEA) Greenhouse Gas Programme and has been completed by the British Geological Survey and Dr Takeshi Ohsumi of CRIEPI. The full scope of the study was the review of natural CO_2 occurrences in a variety of geological settings and comparison of these with some of the processes that may occur over time in man-made CO_2 storage projects. The main processes by which large quantities of CO_2 can be formed in nature by geological processes were identified and some examples of natural CO_2 accumulations that can be considered analogous to current CO_2 storage projects examined. This report focuses on just the volcanic contribution to the global carbon cycle and is intended to provide a reference work for future studies of this nature, the full findings of the IEA commissioned study are reported elsewhere, although that report is bound by client confidentiality.

Acknowledgements

Contents

FIGURES

Summary

Present day geological emissions of CO_2 include both volcanic emissions (both passive, from volcanoes in repose, and those related directly to eruptive activity) and non-volcanic – direct emissions from the Earth's crust and lithosphere. The contribution to the present day atmospheric CO_2 loading from volcanic emissions is, however, relatively insignificant, and it has been estimated that subaerial volcanism releases around 300 Mt/yr CO_2, equivalent to just 1 % of anthropogenic emissions (Morner & Etiope, 2002). Nevertheless, understanding and quantification of Earth degassing is still necessary for understanding the longterm global carbon cycle and the implications of the present day atmospheric CO_2 budget. This report presents a review of volcanic CO_2 emissions in relation to tectonic setting, the different related phenomena, and ultimate source.

1 Introduction

Since the pioneering work of Rubey (1951) which recognised that most volatiles present at the Earth's surface today must ultimately have a volcanic origin, many attempts have been made to quantify the past and present day transfer rates of volatiles from the solid earth to the hydrosphere and atmosphere (Le Cloarec & Marty, 1993). Over geological time the rate of degassing from the Earth is considered to be the major factor controlling the partial pressure of carbon dioxide (CO_2) in the atmosphere and therefore the long-term variations in climate. The amount of gas transferred to the atmosphere in the past (pre-industrialisation) depended ultimately on volcanic activity, which is controlled by (1) the rate of melt (magma) production, (2) the abundance of volatiles in the melt source region[1] and (3) the degree of magma degassing on emplacement (eruption), thus the flux of CO_2 from the solid Earth in the past would have fluctuated in *direct proportion with volcanic activity*. At the present day this is far less significant in comparison with *biological* and more notably *anthropogenic* fluxes. Without the re-supply of CO_2 from geological sources – including volcanic degassing – it has been calculated that removal of CO_2 from the atmosphere by silicate weathering, carbonate deposition and the burial of organic matter could potentially deplete the CO_2 content of the *pre-industrial* atmosphere in 10,000 yrs and the atmosphere–ocean system in 500,000 yrs (Gerlach, 1991). Before the Industrial Era, circa 1750, atmospheric CO_2 concentration had remained fairly stable at 280 ± 10 ppm for several thousand years. It has risen continuously since then, reaching 367 ppm by 1999 (Houghton et al., 2001) and currently stands at around 380 ppm (monitoring station in Hawaii). It can be shown that the present atmospheric CO_2 concentration has not been exceeded during the past 420,000 years, and it is unlikely during the past 20 million years. The rate of increase over the past century is unprecedented, at least during the past 20,000 years. The present atmospheric CO_2 increase is caused by anthropogenic emissions of CO_2. About three-quarters of these emissions are due to fossil fuel burning. Fossil fuel burning (plus a small contribution from cement production) released on average of $23,100 \pm 1.5$ Mt/yr CO_2 in the 1990s. Land use change, increasing urbanisation and deforestation, is responsible for the rest of the emissions. Nevertheless, understanding and quantification of Earth degassing is still necessary for understanding the long-term global carbon cycle and the implications of the present day atmospheric CO_2 budget (Morner & Etiope, 2002).

Geological carbon emissions include both volcanic emissions (both passive, from volcanoes in repose, and those related directly to eruptive activity) and non-volcanic – direct emissions from the Earth's crust and lithosphere. The contribution to present day atmospheric CO_2 loading from volcanic emissions is relatively insignificant, Morner & Etiope (2002) estimate that subaerial volcanism releases around 300 Mt/yr CO_2, representing the equivalent of just ≈ 1 % of anthropogenic emissions. Even during extraordinary times in the geological past, such as the eruption of flood basalts [e.g. the Deccan Traps, 66 Ma], the additional CO_2 emission is estimated to be only 0.3-2 Mt/yr. Nevertheless, the eruption of individual flows would have released significant volumes of CO_2 over very short time periods and such volcanic emissions may have contributed to significant "greenhouse" effects at times in Earth history, and additionally by precipitating of large scale methane hydrate melting (Svenson et al., 2004). Therefore, understanding the impact of such temporary increases on global temperatures may be critical to understanding the impact of present day anthropogenic emissions.

Discussion in the following sections focuses on volcanic emissions, both the processes involved and an attempt is also made at more detailed quantification. Specific examples of different

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[1] Including both CO_2 *and* methane (CH_4), which may be oxidised either during volcanic eruptions or subsequently to release the carbon as CO_2. Whilst most CH4 is biogenic, thus outside the scope of this study, a small proportion of abigenic methane will be released from the mantle during magmagenesis (e.g. Kiyosu & Asada, 1995).

degassing processes are also discussed and case studies of individual volcanic systems presented in Appendices 1-3.
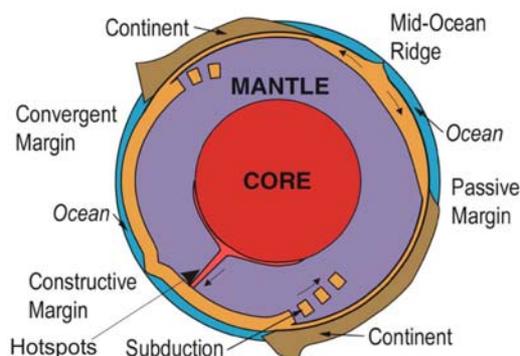
2 Plate tectonics

Figure 1. Schematic cross-section of the Earth, illustrating the structure and its relationship to plate tectonics.

Earth is unique amongst the known planets in the solar system, having active plate tectonics, where a hard, rigid carapace (the crust and lithosphere) is continuously destroyed and recycled into a hot, ductile inner layer (the mantle), Figure 1. Plate tectonics is simply the consequence of the cooling of the planet. Heat was accumulated during the process of accretion some 4.5 billion years ago, and together with the heat generated by the ongoing decay of radioactive nuclides such as U and Th contained within the Earth's core and mantle, its escape drives plate motion. The Earth was obviously much hotter in the geological past and as a result convection was much more vigorous - and there would have been much more volcanic activity. The principle method of heat transfer from deep within the Earth to the surface is via *convection*. Most authors now agree that heat transfer occurs between the core and mantle, and this basal layer then becomes buoyant and rises to the surface due to thermal expansion. At the top of the mantle this material cools, before sinking back into the mantle again. At the top of the mantle lies a rigid, brittle layer, the lithosphere, up to 120 km thick, broken into fragments – the tectonic plates that move relative to one another as a direct consequence of mantle convection. The configurations in which these plates meet results in three types of fundamentally different plate boundaries:

1) *Divergent* or *constructive plate margins* where new lithosphere is formed by magmatic (volcanic) processes along the boundary, the feature formed being termed a spreading centre or rift zone, typically the *mid-ocean ridges* (MORs) characterise these boundaries.

2) *Convergent* or *destructive plate margins*, where the plates collide and typically one plate overrides the other. The feature formed being termed a *subduction zone*, characterised by deep ocean trenches and chains of volcanoes some 250 km onto the over-riding plate, these either forming island chains (volcanic arcs) in the oceanic setting (e.g. the lesser Antillies) or mountain ranges (e.g. the Andes) on the continents. Subduction results in the return of materials from the lithosphere into the mantle.

3) *Transform* or *conservative plate boundaries* where the plates slide horizontally past one another. This type of boundary is characterised by linear fault zones (e.g. the San Andreas Fault).

Volcanism is an intrinsic part of the plate tectonic cycle (Figure 1) and occurs at any point where pressure/temperature conditions are such as to allow partial melting of mantle or lithospheric material. Volcanism occurs at both constructive and destructive plate margins.

At the MORs the mobile mantle material up-wells passively into the void created as the tectonic plates part. As it rises, the mantle material undergoes partial melting in response to

decompression, and the most volatile phases present enter into the liquid phase (magma). This then erupts at the surface to form new oceanic crust.

At convergent plate margins volcanism results from melting of the mantle due to its hydration by volatiles (H_2O, CO_2 etc.) released from the subducted lithospheric slab (tectonic plate). The melting point of the overlying mantle material is reduced with increased volatile content. Pressure-temperature-dependent breakdown of hydrous mineral phases in the subducted lithospheric material as it descends is commonly invoked to explain the release of volatiles.

Volcanism also occurs at apparently random locations, sometimes at great distance from the plate margins. This is referred to as *intraplate* or *hotspot* volcanism. These are also an integral part of the plate tectonic cycle and are generally accepted to be the surface manifestation of up-welling of the hot, buoyant material from the core-mantle boundary.

The most important consequence of plate tectonics in this context is the geological recycling of materials – elements, including carbon. Volcanism plays a crucial role in this process. The flux of primary (juvenile[2]) carbon out gassed over geological time has supplied the surface reservoirs, and out-gassing of primary material continues to accompany volcanic activity. It is, however, now the consensus that the contribution of juvenile CO_2 to the total flux is minor and that recycling and degassing of crustal carbon is an integral part of the plate tectonic cycle.

3 Gaseous emissions from volcanoes: source and compositional variations

Whilst H_2O is consistently the dominant gas emitted by volcanoes (normally making up >60% of the total molar gas content) CO_2 is the next most abundant species and typically constitutes 10-40% of the vapour phase (Delmelle & Stix, 1999). Magmatic gases can be introduced into volcanic emissions from various sources at depth including the convecting mantle, lithosphere (crust and uppermost part of the mantle) and subducted slab material. Given that these sources are chemically distinct, the composition of the vapour phase emitted from volcanoes will vary depending on the tectonic and geological setting. Both the chemical and isotopic signatures of the volcanic gases can be used to determine their ultimate sources. Gases from volcanoes at convergent plate boundaries have proportionally more H_2O and HCl than those at divergent plate boundaries or hotspots.

There are also significant variations in the gaseous phase compositions within the tectonic groups discussed above, some of which can be attributed to differing gas solubilities in the magma, CO_2 being the least soluble of the major magmatic volatiles [HF>HCl≈H_2O>S-phases>CO_2], implying early degassing of CO_2, and that with time, if there is no fresh supply of magma at depth, gaseous emissions may evolve from proportionally CO_2 rich to CO_2 poor (Delemelle & Stix, 1999).

Stable isotopes can also be used to infer the deep sources by assuming isotopic compositions for earth's surface reservoirs (see section 4). In this way the isotopic compositions $\delta^{13}C$ [and $\delta^{34}S$] indicate a mantle source for both divergent plate boundaries and hotspot volcanoes. The relationship between CO_2 and He abundances and isotopic compositions have also been used to place limits on upper mantle C-contents and on the fate of C recycled at subduction zones (Trull et al., 1993). They conclude that the upper mantle carbon content must be < 500 ppm C and is probably in the range 50-250 ppm. Additionally significant C-recycling into the upper mantle source tapped by MORs is ruled out, although data are found consistent with recycling into the

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[2] Juvenile gas – a volatile phase that was formed or present during the initial accretion of the earth; subsequently degassed to the surface over time.

lower mantle source (generally accepted to be a layer at the core-mantle boundary) tapped by hotspot volcanism.

4 Isotope systematics and carbon sources

Stable isotope ratios of carbon [and sulphur] present in volcanic gas emissions can be used to infer a magmatic or biogenic source for volatiles, and characterise multiple deep reservoirs for magmatic volatiles [and respective contributions]. These inferences are based on the assumed isotopic compositions of the Earth's surface reservoirs of these elements. A CO_2 molecule can have different molecular weights as a result of the presence of one of the two stable carbon isotopes ^{12}C or ^{13}C and/or one of the three stable isotopes of oxygen, ^{16}O, ^{17}O or ^{18}O. Carbon isotope data from CO_2 are usually expressed relative to the PDB standard. The PDB standard is the ratio of ^{12}C to ^{13}C in parts per thousand compared to those found in carbon in the belemnite *Belemnitella americana* from the Late Cretaceous, PeeDee Formation, in South Carolina. The unit used to express this is $\delta^{13}C_{CO_2}$ PDB, values are quoted per mil (‰). The range of $\delta^{13}C_{CO_2}$ PDB values found in a sample of CO_2 can help distinguish its origin. In addition to stable carbon isotopes, the unstable isotope of carbon, ^{14}C, can help identify the source of carbon dioxide. It is continually being created in the Earth's atmosphere at what is thought to be a constant rate and is incorporated into carbon compounds in living organisms. It has a half life of 5730 years and can be used to date material less than 50,000 - 100,000 years old. The presence of significant amounts of ^{14}C in CO_2 indicates that it has a relatively recent origin.

The isotopic composition of carbon measured in CO_2 emissions from high temperature gas emissions at divergent plate boundaries (e.g. Etra-Ale, Ethiopia) and Hotspots (e.g. Kiluaea, Hawaii) indicate a purely mantle origin for the carbon ($\delta^{13}C$ = -4.0 ± 2.5 ‰). In contrast, subduction related high temperature gases display more variable $\delta^{13}C$ (& $\delta^{34}S$) values –12 to +2.5 ‰), indicating input from crustal and subducted crustal materials. Isotopic inferences are also reinforced by the observation at the Popocatépetl volcano (Mexico) of xenoliths of metamorphosed carbonate rocks containing wollastonite and other calc-silicate minerals indicating reaction of magma with Cretaceous limestone underlying the volcano in its eruptive products (Goff et al., 2001).

The helium content of the volcanic gas emissions may also be used as a reference. Subduction zone emissions show very high CO_2:He ratios, 3-15 times those at divergent plate or hotspot settings and the excess CO_2 is attributed to input from the subducted slab. Helium isotopes; ^{3}He and ^{4}He can also be used to infer volatile sources. Radioactive decay of U and Th yield ^{4}He. The only source of ^{3}He (primordial He) is therefore the deep mantle and core, given that He is rapidly lost from the atmosphere on release from the solid Earth due to its low atomic mass. Based on the $\delta^{13}C$ and $CO_2/^3$He ratios measured in volcanic gases from convergent plate boundary volcanic centres, it can be inferred that up to 80 % of arc volcanic CO_2 is recycled, exogene carbon derived from subducted (lithospheric) material, with a relatively small input from the convecting (asthenospheric) mantle (Varekamp et al., 1992). This figure can reach >90%, however, where two arcs collide (Jaffe et al., 2004). The remainder is derived from a MOR-type mantle reservoir (Sano & Marty 1995). The sum of globally deep-subducted sediment and slab carbon exceeds the estimated arc CO_2 flux, and Varekamp et al. (1992) calculated that approximately 3.5 teramole of carbon must return annually to the mantle in convergent zones. These authors also calculate that the combined processes of modern MOR volcanism, slab alteration, and subduction zone volcanism do not produce a substantial carbon flux into the exosphere. Carbon is recycled into the deep mantle via subduction of carbonate: limestones and carbonate veins in oceanic crust (Wallace & Anderson, 1999). This has increased over the last 180 my with biological evolution (primarily the evolution of calcareous nanoplankton in the Jurassic), causing an increase in the production of lime sediments, possibly even reversing the

flux of CO_2 from crust to mantle *prior to industrialisation*. Carbonate, if mixed with quartzose material will undergo de-carbonation leading to release of CO_2 at relatively shallow depth which then escapes to the surface. Carbonate rocks alone may remain stable allowing subduction into the mantle. Dolomite is stable at mantle depths and in regions where dolomite is stable, CO_2 is relatively soluble in silicate melts and may flux partial melting at relatively low temperatures. The resulting CO_2-rich magmas then ascend, degassing at shallow depths. Trull et al. (1993) note that recycling of carbon to the lower mantle (via subduction) is also consistent with observed C-He systematics and can account for both the similarity of ridge and hotspot carbon isotopic compositions and the low exospheric C inventory, whilst at convergent plate margins, the C/He ratios are vastly increased over hotspots.

In regions of active volcanism, the presence of magmatic carbon dioxide (CO_2) in regional hydrologic systems may also provide a radiocarbon-depleted tracer for delineating ground-water transport and mixing processes (Rose & Davisson, 1996).

5 Present day volcanic carbon flux estimates

Terrestrial volcanism occurs within both the hydrosphere and atmosphere. Submarine and subaerial volcanism originate almost entirely within different tectonic environments (as outlined above), tapping different, although not entirely exclusive volatile sources, shown schematically in Figure 2, below.
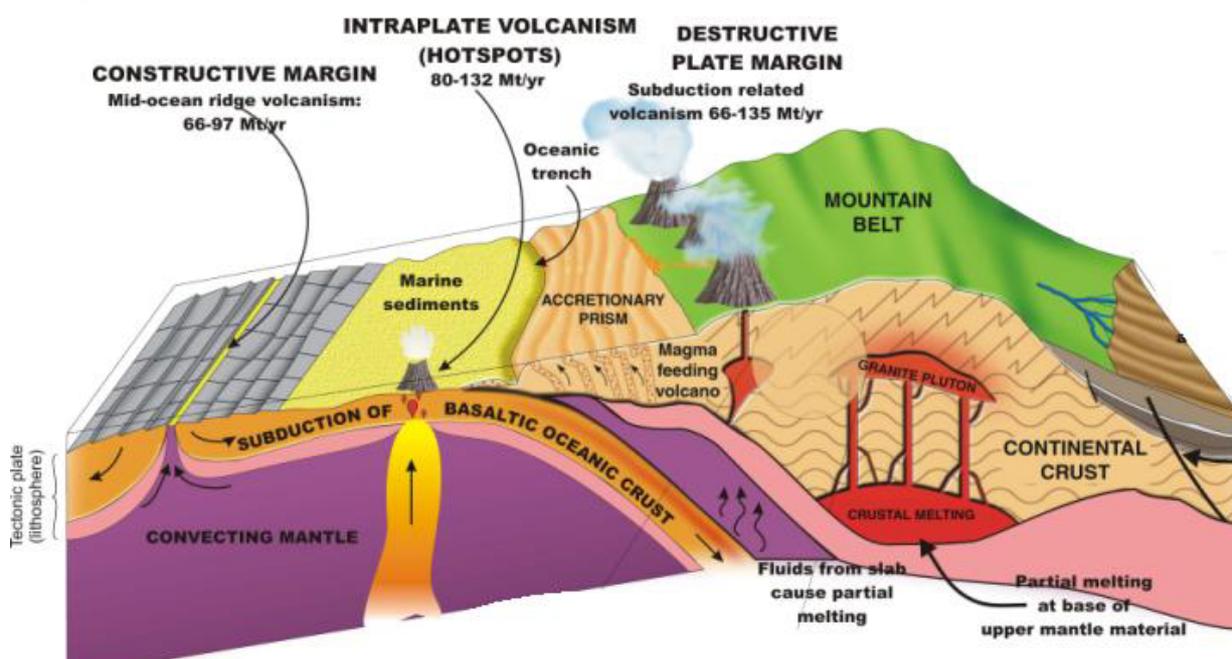
Figure 2. Diagrammatic representation of the different volcanic environments with estimates of CO_2 emission rates and their relationship to plate tectonic environment.

Submarine volcanism occurs almost entirely (>90%) along the MORs, and can be considered to have been relatively constant over the recent past [Quaternary period] when the extrusion rate has been estimated at 20 km^3/yr (Le Cloarec & Marty 1993), Marty & Tolstikhin (1998) computed the C-flux at MORs to be 97 ± 40 Mt/yr, in agreement with Holloway & O'Day's (2000) 97 Mt/yr. Morner & Etiope (2002) subsequently reviewed published estimates for the global MOR CO_2 flux and report a range from 66 to 97 Mt/yr. These authors also observe that this appears balanced by the sink provided by hydrothermal alteration of the newly formed ocean floor lavas. It can therefore be assumed that changes in volcanic CO_2 fluxes generated by changes in the rate of ocean floor formation at MORs have little effect on the atmospheric CO_2

budget at the present day. Additionally, H_2 is produced during the eruption of MOR lavas by the reduction of H_2O by ferrous iron in the magma to form magnetite. Holloway & O'Day (2000) have calculated that 277 Mt/yr H_2 could be released during degassing and crystallization of MOR lavas, about three times greater than the calculated annual CO_2 production [97 Myt/yr]. Given that the annual CO_2 production rate from MOR lavas of over 3.3 Ga can account for all CO_2 found in the Earth's crust, hydrosphere, and atmosphere, it is likely that the H_2 produced at mid-ocean ridges plays a significant role as a reducing agent in the global redox state of the Earth's surface. Additionally, observations indicate that MOR lavas are emplaced in numerous short pulses of dyke intrusion accompanied by lava flows over very short time periods resulting in the rapid release of CO_2 and H_2 which may result in formation locally of a separate gas phase containing H_2-CO_2-H_2O in that order of abundance. Holloway & O'Day (op. cit.) suggest that this could provide a significant energy source for autotrophic microorganisms.

It has been proposed (Dessert et al., 2003) that the surface area of continental basalts plays a major role in the carbon cycle as a C-sink, and these authors estimate that around 180 Mt/yr CO_2 is consumed in the basalt weathering process, which must be subtracted from the published estimates of volcanic output to obtain a true [net] value for volcanic contribution to the atmospheric CO_2 budget.

The vast majority of subaerial volcanoes lie in volcanic arcs above subduction zones, and although they representing just 10-20 % of volcanism on earth, these volcanoes have the greatest societal impact, and proportionally release the greatest amount of CO_2. Nevertheless, there is also lesser input from hotspot (intraplate) volcanism. The CO_2 production rate from the more sporadically active subaerial volcanoes is more difficult to estimate than MORs, and estimates are based on direct measurements from relatively few volcanoes. Nevertheless, subaerial volcanoes typically emit 0.1-2 Mt/yr CO_2, and the highest emission rates seem to be associated with alkaline volcanic systems. Mt Etna (discussed in more detail in Appendix 2), is Europe's largest active volcano also the most actively degassing (25 Mt/yr CO_2; Allard et al., 1991). This has been attributed in part to the de-carbonation of limestone and dolomite on the platform on which Etna lies, in addition to the alkaline nature of the magma (Gerlach, 1991). Nevertheless, recent estimates suggest Popocatépetl, may be the most actively degassing volcano, emitting up to 36.5 Mt/yr CO_2 (Morner & Etiope 2002).

The total production rate for all sub-aerial volcanism has been estimated to be < 6 km^3/yr, ≤ 30% of the global output (Le Cloarec & Marty, 1993). Estimates of CO_2 emissions from subduction-related volcanism range from 66 to 135 Mt /yr and for hotspot volcanism from 80 to 132 Mt/yr including both eruptions and passive degassing based on either direct sampling or C/^{3}He ratios (Morner & Etiope, 2002).

6 Emission of CO_2 during explosive volcanic eruptions

Volatiles are a fundamental part of volcanic activity and play a critical role in determining the behavior of the volcano. Increasing availability of volatiles results in increasingly explosive activity (Delemelle & Stix, 1999). Explosive eruptions can inject large amounts of volcanic gases into the atmosphere. The reactive gas species may be scavenged by hydrometeors within the eruption column, and high uncertainties remain regarding the proportion of volcanic gases, which eventually reach the stratosphere (Textor et al., 2003), however, a significant proportion of erupted CO_2 is likely to survive. In the twentieth century, the most significant eruptions were that of Katmai, Alaska, in 1912, followed by Mt Pinatubo in 1991, which in turn was 10 times larger than the eruption of Mount St. Helens in 1980. Climatic effects – due to aerosol injections into the stratosphere - have been documented for the more recent two examples.

Whilst it has been demonstrated above that volcanic CO_2 represents a relatively insignificant proportion of the total annual flux reaching the atmosphere, pulses in subaerial volcanism may

have short-term impacts on the atmospheric CO_2 budget. Such volcanism can contribute both directly and indirectly to the global carbon cycle, directly through the introduction of CO_2 into the atmosphere, and indirectly by introducing ash and aerosols; although unless these are injected into the stratosphere, they have little effect. Stratospheric injection is most likely to occur at high latitudes, where the troposphere is at its thinnest (Hay, 1996). Short-term variations in climate have frequently been attributed to volcanic activity, both through the increased "greenhouse effect" due to increased CO_2 content of the atmosphere and the increased amount of diffuse radiation reaching the Earth's surface due to the presence of stratospheric aerosol increasing photosynthetic processes and the uptake of carbon by vegetation. Such enhancement of the terrestrial carbon sink could temporarily result in a decline in the growth rate of atmospheric carbon dioxide after an eruption, sufficient to cancel out greenhouse warming from a doubling of carbon dioxide (Dickenson, 1996)[3].

The CO_2 from such major eruptions does not pose a danger (independent from that of the explosive eruption itself) to man or the local natural environment. Much of the gas emitted in such eruptions is extremely hot and is carried upwards into the upper parts of the atmosphere where it disperses by mixing with the ambient air.

7 Diffuse, flank degassing and CO_2 emissions from subaerial volcanoes

Magmatic gases are released rapidly from the central conduit(s) of volcanoes during violent eruptions, as described above. Only recently has it been recognised that quiescent, non-eruptive, diffuse degassing may be the principle mode of gas release from many volcanoes. Diffuse emissions of CO_2 are known to be large around some volcanoes and hydrothermal areas (Evans et al. 2001). Gases can percolate to the surface through porous zones on volcano flanks. Gases emitted in this manner are generally non-reactive, and do not contain highly acidic species such as SO_2, HCl, and HF, and also tend to be emitted at low temperatures, often through the soil and through springs. The main gases emitted in this manner are CO_2 and He. Diffuse emissions of CO_2 are known to be large around some volcanoes and hydrothermal areas, although published estimates of these emissions vary dramatically. At present there is no real consensus about the relative importance of this mode of degassing and its full contribution to atmospheric loading (Delemelle & Stix, 1999) and, to date, diffuse emissions of CO_2 have only been studied in any detail on a limited number of volcanoes. Nevertheless, as more studies have been made of these emissions, the importance of faults and fractures in degassing has become increasingly apparent, and the presence or absence of faults with surface expression appears to be the principle control on whether a volcano can degas through its flanks, in addition to established summit craters or vents.

Diffuse flank degassing can also be significant on active volcanoes. For example, diffuse emissions from the upper flanks of Mt. Etna, Sicily (Appendix 2) appear to be of similar magnitude to those emitted from the crater plume, and the isotopic composition ($\delta^{13}C$ and $^3He/^4He$) of these emissions is consistent with a mantle, i.e. magmatic, origin, (e.g. Allard et al., 1991). Flank emissions have visibly resulted in areas of dying forest and incidents of near asphyxia in confined spaces. In 1994 Farrar et al. (1995) recorded CO_2 concentrations of 30-96%

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[3] It should also be noted that volcanoes also release subordinate amounts of SO_2 (Delemelle & Stix, 1999), which is oxidised by moisture in the atmosphere to produce sulphate aerosols. Sulphate aerosol forcing tends to have a cooling effect on the atmosphere in contrast to greenhouse gases like CO_2, most notably on a regional scale, although compared to greenhouse gas forcing, sulphate aerosol forcing is far less certain, due to limited understanding of the radiative properties of these aerosols and their effect on clouds (Jones & Mann, 2004). Detailed discussion of sulphate aerosols or SO2 emissions is, however, beyond the scope of this report.

were recorded in a 30-hectare area of tree kill on the quiescent Mammoth Mountain volcano, California, and a total CO_2 flux of $\geq 1, 200$ t/d. Whilst the tree kill coincided with the episode of shallow dyke intrusion, the magnitude and duration of the CO_2 flux indicates that a larger, deeper magma source and/or a large reservoir of high-pressure gas is being tapped (see Appendix 2). The results of studies of plant responses to the *slightly* elevated CO_2 concentrations found around springs in many volcanic regions are also summarised in Raschi et al. (1997).

A further example is the Yellowstone geothermal area, where surface measurements have suggested that some 1.6 ± 0.6 Mt/yr CO_2 is released from due to diffuse degassing (Werner & Brantley, 2003). This is comparable to the CO_2 contribution from other large subduction-related volcanic systems and the combined contribution from the Hawaiian hot spot.

Diffuse emissions from the flanks [in addition to emissions from the summit craters/vents] of active volcanoes can also be significant; best illustrated when estimates for volcanic CO_2 emissions from Mt Etna are considered (Allard et al., 1991; see Appendix 2).

Whilst diffuse flank degassing appears significant on many volcanoes, by no means all volcanoes degas in this way, and those that do may show intermittent periods of flank degassing. The overall control appears to be the structure and stress-field of the region. This is illustrated at Popocatépetl, where the current phase of activity began in December 1994. Whilst the volcano is actively degassing from its summit crater, there is no evidence of an active geothermal system or a diffuse gas component on the volcano's flanks (Varley & Armienta, 2001). Similarly at Kilauea, Hawaii's most active volcano during historical time - latest eruption beginning January 1983, a CO_2 emission rate of 8500 t/d has been recorded from the summit, comprising the bulk of the volcano's emissions ($\approx$ 9000 t/d; Gerlach et al., 2002).

Quantification of diffuse emissions is arguably a major issue when attempting to estimate the global emission rate of CO_2 from subaerial volcanism, and with the present paucity of data, remains extremely difficult. Nevertheless, Morner & Etiope (2002) estimate that the emissions from the 500 or so historically active sub-aerial volcanoes would amount to 250 Mt/yr, adding diffuse degassing for which they present a conservative estimate of ~50 Mt/yr, giving a total emission rate of 300 Mt/yr; the effective contribution of subaerial volcanic activity to CO_2 emissions to the atmosphere.

8 Sudden emissions of CO_2

Rapid emissions of volcanic gas also occur episodically during periods of apparent quiescence. The gas is predominantly CO_2 with trace amounts of other non-reactive gases (e.g. N_2, CH_4 and noble gases such as He). Whether the released CO_2 is derived directly from degassing due to depressurisation of new magma entering the shallow subsurface, or whether it is the result of the disturbance of a pre-existing reservoir by the seismic activity accompanying the magma injection, is the subject of debate. The presence of gas reservoirs beneath volcanoes has been inferred from the presence of shallow seismic anomalies which have been interpreted as porous, gas-filled rock at Mammoth Mountain (Foulger et al., 2003) and the Yellowstone volcanic field - another example of an area of diffuse degassing during a period of volcanic quiescence (Husen et al., 2004). The presence of large CO_2 reservoirs at shallow depths means that many apparently quiescent volcanoes may be a risk for rapid expulsions of CO_2 volumes far exceeding that which could be derived from the magma volumes erupted during volcanic eruptions.

Both hot and cold springs are a common feature in volcanic regions and diffuse degassing may result in significant amounts of gas becoming dissolved in the local groundwaters, from which these springs rise. An example of this was documented at the Albani Hills, Italy, where >0.2 Mt/yr CO_2 rises from the depths and subsequently dissolves into shallow groundwater (Chiodini & Frondini, 2001), which can become oversaturated. The presence at shallow level of CO_2-

oversaturated groundwater can explain several episodes of sudden gas release in the area, which has been documented by historical chronicles since Roman times.

About 16% of Holocene or younger volcanoes contain lakes, with a higher percentage in volcanic arcs (Delemelle & Bernard, 1999). Many are hot and contain large amounts of dissolved solids, however, three have documented as containing large amounts of potentially lethal gas – predominantly CO_2 - in their lower waters. Sudden escape of this gas occurred from lakes Monoun and Nyos, two lakes in maar craters along the Cameroon volcanic line in Western Africa (See Appendix 3; 1), in August 1984 killing 37 and August 1986 killing more than 1,700 people respectively by suffocation resulting in a raising awareness of the phenomenon (Freeth et al., 1990). Both lakes constitute "unusual" environments, being both chemically and thermally stratified with the capacity to accumulate tremendous amounts of free CO_2 dissolved by pressure in the bottom layer, and non-eruptive diffuse emission provides a mechanism by which significant amounts of CO_2 may be injected into crater lakes (Allard et al., 1991, Gerlach, 1991). The CO_2 release from Lake Nyos is attributed to overturn of the stratified lake waters resulting in runaway exsolution dissolved gas – a process which has subsequently been refered to as a limnic eruption", a term was first coined by J.C. Sabroux at the UNESCO Conference on the lake Nyos disaster, in March 1987 at Yaounde, in order to take into account the analogy with volcanic eruption, (also powered by gas bubbles ascending and expanding in a liquid - the magma). Once CO_2 bubbles nucleate within a saturated layer of the lake water, they rise and grow, attracting in their wake deeper water available for ex-solution, feeding the chain reaction process: the entire lake overturns through an ascending column of rising and expanding bubbles (Zhang, 1996). Geochemical evidence points to the Cameroon volcanic line being a zone of enhanced mantle degassing, and diffuse emissions being fed directly into the lake via thermal springs (Kusakabe et al., 2000). Calculations show that Lake Nyos contained 0.5×10^6 tons CO_2 in its waters (Delemelle & Bernard, 1999).

A further example of rapid gas release is the Dieng volcanic complex in Java (Appendix 3; 2). In 1979, 149 people were killed by a *poisonous gas* (shown to be predominatly CO_2) eruption. Then again in1992, sudden emission of gas killed one person and hospitalized two others.

The visible results of rapid emission of large volumes of CO_2, such as deaths by asphyxiation and tree-kills, have raised awareness of volcanic CO_2 emissions in recent years. Nevertheless, the attention given to these high-profile events is disproportionate to their actual significance in terms of the global atmospheric CO_2 budget.

Appendix 1 Emissions of CO$_2$ during explosive volcanic eruptions

A1.1 THE ERUPTION OF MOUNT PINATUBO, 1991

Mount Pinatubo, located in the Philippines, [15.13º North, 120.35º East] is one of a chain of composite volcanoes that constitute the Luzon volcanic arc. The arc parallels the west coast of Luzon and reflects eastward-dipping subduction along the Manila trench to the west. Mount Pinatubo is among the highest peaks in west-central Luzon. Its former summit, at 1,745 m elevation, may have been the crest of a lava dome that formed about 500 years ago, although this was reduced to 1,485 m (high point caldera rim) during the most recent previous major eruptive episode (Wolfe & Hoblitt, 1996). The 1991 eruption marked the re-awakening of a volcano after a 500-year period of quiescence. During the climactic eruption a giant ash cloud rose 35 km and injected a minimum of 17 Mt SO$_2$ into the stratosphere – the largest stratospheric SO$_2$ cloud ever detected, and more than an order of magnitude more SO$_2$ than could have been dissolved in the 5 km^3 of erupted dacite at pre-eruptive conditions. Experimental studies, geobarometer results and the H$_2$O and CO$_2$ contents of glass inclusions indicate that the magma was saturated with a water-rich vapour prior to its ascent and eruption, and modelling of the vapour composition suggest that volatile emissions derived from this pre-eruptive vapour phase also included *at least* 42 Mt CO$_2$ (Gerlach et al., 1996). In comparison it can be estimated from fumarolic gas compositions and SO$_2$ emissions (Casadevall et al., 1983), that CO$_2$ released during the 18 May 1980 eruption of Mt. St. Helens was between 4.8 and 22 Mt.

Gu et al. (2003) documented the effects of the volcanic aerosols from the 1991 Mount Pinatubo eruption which greatly increased diffuse radiation worldwide over the following 2 years, and estimated that the increase in diffuse radiation enhancing noontime photosynthesis of a deciduous forest by 23 % in 1992 and 8 % in 1993 under cloudless conditions.

Appendix 2: Examples of diffuse flank CO_2 emissions

A 2.1 MAMMOTH MOUNTAIN, CALIFORNIA, USA

Mammoth Mountain, in central eastern California, USA, is a large volcano with a long history of volcanism that began some 200,000 years ago and produced phreatic eruptions as recently as 700 ± 200 years ago, although it currently displays only weak fumarolic activity and no summit activity (Farrar et al., 1995; Sorey et al., 1998). Areas of tree kill (and/or heavier than normal needle drop during the summer months) began to appear around the volcano in 1990, around the same time as a reported incident of near-asphyxia in confined spaces; indicative of an increase in diffuse flank emissions of CO_2, such as have also been recorded at Mount Etna and Vulcano (Allard et al., 1991). CO_2 and He with isotopic compositions indicative of a magmatic source ($\delta^{13}C$ = -4.5 to –5 ‰, $^3He/^4He$ = 4.5-6.7 times atmospheric) have been found to be discharging at anomalous rates, as cold soil gas emissions from steam vents and dissolved in groundwaters both prior to and subsequent to the tree kills. Nevertheless, the rate of gas discharge increased significantly in 1989 following a 6-month period of persistent earthquake swarms and associated strain and ground deformation attributed to dyke emplacement beneath the mountain. Additionally, an increase in $^3He/^4He$ in vapour discharged from a fumarole on the north side of the mountain (Sorey et al., 1998; Sorey et al., 1993) reinforced the inferred presence of new magma beneath the area. Tree kills presently affect an area of some 360,000 m^2, which is additionally characterised by diffuse cold soil CO_2 emission. A soil gas survey, begun in 1994, revealed CO_2 concentrations of 30-96 % in the area of the tree kills (Farrar et al., 1995). The total area affected by diffuse CO_2 degassing on Mammoth Mountain is about 480,000 m^2 (Gerlach et al., 2001). Both the tree-kill areas and a further notable area of CO_2 discharge above the tree line occur in close proximity to fault zones, which may provide conduits for gas flow from depth. It has been estimated that the total diffuse CO_2 flux from the mountain is approximately 520 t/d, and that a further 30-90 t/d of CO_2 are dissolved in cold groundwater flowing off the flanks of the mountain (Evans et al., 2002; Gerlach et al., 2001). Magmatic CO_2 discharge through cold groundwaters is thought to represent a significant fraction of the carbon discharge globally from volcanoes.

The compositional (isotopic and chemical) homogeneity of both soil and fumarolic gases suggest a common gas reservoir whose source is probably a combination of magmatic degassing and thermal metamorphism of metasedimentary rocks (Sorey et al., 1998). Whilst the onset of tree kill coincided with the episode of shallow dyke intrusion, the magnitude and duration of the CO_2 flux indicates that a larger, deeper magma source and/or a large pre-existing reservoir of high-pressure gas has been tapped throughout (Farrar et al., 1995). The presence of a gas reservoir is reinforced by the presence of a seismic (low-V-p/V-s) anomaly extending from the surface to ~1 km below sea level beneath the region (Foulger et al., 2003). Temporal variations in structure beneath Mammoth Mountain showed that significant changes in both V-p and V-s were consistent with the migration of CO_2 into the upper 2 km or so beneath Mammoth Mountain and its depletion in peripheral volumes that correlate with surface venting areas. It would also suggest that should the area be subject to higher magnitude earthquake activity, a more rapid, high volume escape of gas could result. Episodes of increased emission rates have been recorded on a number of occasions; e.g. during 1997 at Horseshoe Lake (McGee et al., 2000), at which time direct degassing from a shallow intrusion of new magma is considered implausible since the released gas was cold and barren of other magmatic gases (except He). McGee et al. (op cit) propose that increased compressional strain on the area south of Mammoth Mountain, driven by movement of major fault blocks in the Long Valley caldera at this time, was responsible for triggering the increased degassing from the reservoir to the surface via faults and other structural weaknesses. Nevertheless, recharge of the gas reservoir by CO_2 emanating from the deep intrusions that probably triggered deep long-period earthquakes may also have contributed to the 1997 degassing event.

Although the CO_2 is thought to migrate from a reservoir towards the ground surface via faults and fractures, which are essentially linear features in plan view, the nature of CO_2 discharge at the soil-air interface is more diffuse because it is dispersed within the porous High Sierra soils and by meteorological processes (McGee et al., 2000; Rogie et al., 2001).

A2.2 MOUNT ETNA, SICILY

Mount Etna, in Sicily [37.734°N , 15.004°E], is Europe's highest volcano, reaching 3350 m above the city of Taormina on its NE flank. From a structural point of view, the volcano lies above the boundary between the Eurasian and African plates in the central Mediterranean. Etna has one of the world's longest documented historical records, dating back to the 2nd millenium BC. Historical lava flows cover much of the surface of this massive, 60×40 km wide basaltic stratovolcano, and extend to the sea. Persistent explosive eruptions, sometimes with minor lava emissions, take place from one or more of the three prominent summit craters. Flank vents, typically with higher effusion rates, are less frequently active and originate from fissures that open progressively downward from near the summit (usually accompanied by Strombolian eruptions at the upper end). Cinder cones are commonly constructed over the vents of lower-flank lava flows. Lava flows extend to the foot of the volcano on all sides and have reached the sea over a broad area on the SE flank.

Etna is also one of the world's most actively degassing volcanoes (Allard et al., 1991; Gerlach, 1991), and large quantities of CO_2, H_2O, SO_2 and other species are released from the summit crater; CO_2 output has been calculated at 13 ± 3 Mt/yr (Brantley & Koepenick, 1995; D'Alessandro et al., 1997). Large amounts of CO_2 have been observed escaping from the volcano's flanks; estimates of the mass of flank emissions vary from 1 to 13 Mt/yr (Delemelle & Stix, 1999). Additional CO_2 is dissolved in Etna's aquifers and it has been estimated that approximately 0.25 Mt/yr escapes this way (D'Alessandro et al., 1997). Study of the carbon isotope composition ($\delta^{13}C$) of the CO_2 and He isotopic ratios from both the flank and summit emissions on Etna suggest a minor contribution of organic carbon, whilst at the most active sites of gas emission, the isotopic data are consistent with a mantle origin for both gases (De Gregorio et al., 2002). The spatial distribution of soil gas anomalies have also been studied over a wide area (approximately 110 km^2) on the SW flanks of Mt. Etna by De Gregorio et al. (2002), and the highest soil emissions were found to delineate the existence of an active fault system.

A2.3 YELLOWSTONE VOLCANIC FIELD, WYOMING, USA

The Yellowstone volcanic field [44.43°N, 110.67°W] has developed through three volcanic cycles spanning two million years that included some of the world's largest known eruptions. It is underlain by the Yellowstone hotspot, recent manifestations of which have included volcanism, active crustal deformation, extremely high heat flow (about 30 times the continental average), and intensive earthquake activity (Smith & Braile, 1994). Voluminous (1000 km^3) lava flows have been erupted within the Yellowstone caldera over the last 150,000 years. Nevertheless, no magmatic eruptions have occurred historically, although phreatic eruptions have occurred near Yellowstone Lake and the most recent activity is thought to have occurred around 1050 BC. Yellowstone is presently the site of one of the world's largest hydrothermal systems including Earth's largest concentration of geysers, and active degassing continues.

Surface measurements suggest that 1.6 ± 0.6 Mt/yr CO_2 are released from Yellowstone due to diffuse degassing, comparable to the CO_2 contribution from other large subduction-related volcanic systems and the combined contribution from the Hawaiian hot spot (Werner & Brantley, 2003). Likewise, the CO_2 flux from Yellowstone (on average 0.0001 Mt CO_2 per km^2/yr) is comparable to other large volcanic and hydrothermal systems worldwide. Analyses of carbon and helium isotopes suggest that around 50 % of the CO_2 emitted is derived from sedimentary sources at locations outside the caldera, whereas locations inside the caldera have a

lower contribution from sedimentary sources (< 30 %). Earthquake tomography suggests a volume of porous, gas-filled rock is located at shallow depths of < 2.0 km in the northwestern part of the Yellowstone volcanic field (Husen et al., 2004). The close spatial correlation of the observed anomalies and the occurrence of the largest earthquake swarm in historic time in Yellowstone (1985) additionally suggest that this gas may have originated as part of magmatic fluids released by crystallization of a body of magma lying beneath the Yellowstone caldera.

Appendix 3: Examples of sudden, rapid emissions of volcanic CO_2

A3.1 THE OKU VOLCANIC FIELD, CAMEROON EMISSIONS OF CO_2 FROM CRATER LAKES: LAKE NYOS AND LAKE MONOUN

The Oku volcanic field [6.25°N, 10.50°E] lies on the southwest trending 1,600 km long Cameroon volcanic line, Western Africa and comprises numerous maars and basaltic cinder cones on or near the deeply dissected rhyolitic and trachytic Mount Oku stratovolcano (3011 m). The central massif is cut by a large caldera (http://www.volcano.si.edu). The Oku volcanic field is best known for two lakes, Lake Monoun to the south and Lake Nyos to the north, lying in young maar craters. Lake Nyos has a surface area of 1.8 km^2, a flat bottom, and a maximum water depth of 208 m. Lake Monoun, is 1.5 km across east to west and 0.5 km north to south, and is also up to 100 m deep. Both lakes drew the attention of the world media in the 1980's when they were the sites of catastrophic "limnic eruptions" or sudden violent carbon-dioxide gas release events. On the evening of 21st August 1986 a large amount - around 1 km^3 - of CO_2 gas erupted from Lake Nyos. The gas subsequently covered the local villages in the downstream area along the valley, resulting in the deaths of 1746 inhabitants and a large number of livestock. The emission of CO_2 was at the time attributed either to overturn of stratified lake waters as a result of a non-volcanic process, or to phreatic explosions or injection of hot gas into the lake (Kling et al., 1987). In August 1984, a similar, but smaller scale gas outburst occurred at Lake Monoun, resulting in the deaths of 37 people (Sigurdsson et al., 1987).

The CO_2 content of the water in Lakes Nyos and Monoun has been found to increase with the depth and a large amount of CO_2 gas remains in the deep watermass, and chemoclines can be identified at the depths of 50.5 m and 188 m in Lake Nyos. The striking feature of the profile is the evolution with time of temperature, electric conductivity and H_2CO_3 concentration in the bottom water at depths below 180 m indicate a common source of heat, salinity and CO_2, most probably the result of CO_2-rich hot spring waters with high salinity feeding directly into the lake bottom. Because of strong stratification of the water column, the incoming fluids are trapped in the deepest water layers. (Kusakabe et al., 2000) estimated the supply rate of CO_2 at the bottom of Lake Nyos from the time evolution of the CO_2 profiles, and concluded that the present rate of CO_2 supply to the lake water was 100 ± 50 x10^6 mole/yr (4400 tonnes per year). Isotopic data from dissolved gases in Lake Nyos [and Lake Monoun, Lake Kivu and other volcanic lakes] indicates that the CO_2 is predominantly derived from the mantle and mixed with a small amount of air and the gas derived from limestone decomposition (Kusakabe 2002).

Based on this geochemical evidence, it is now the consensus that the gas eruption was caused by self-accelerating spontaneous gas exsolution from the lake water, dubbed a "*limnic eruption*" given that the CO_2 would have been stored in the lake's hypolimnion (Kusakabe et al., 1989). Kusakabe (2002) presented CO_2 profiles at Lakes Monoun, and Nyos [and Kivu], the common feature amongst which was that water is well mixed below the chemocline (seen as a shoulder of the CO_2 content vs. depth [pressure] profiles). When this shoulder reaches the CO_2 saturation curve the stratification will become critically unstable and CO_2 may be released. Any external turbulences could then result in destabilisation and rapid [runaway] exsolution of CO_2. To predict gas outbursts in these lakes therefore requires an understanding of the development of the density structure. The stratification of the water column is due to the differential diffusion of CO_2 and heat, CO_2 solubility is limited by temperature, but increases with pressure. The stability of such a "time bomb" stems from the fact that CO_2-rich water is denser than pure water, *as long as gas bubbles do not nucleate*. Given the continuing heat input the stratification intrinsically unstable. Once CO_2 bubbles nucleate within a saturated layer of the lake water, they rise and grow, attracting in their wake deeper water available for ex-solution, feeding the chain reaction process and resulting in the rapid ascent of a column of rising and expanding bubbles. Thus

monitoring of the CO_2 content of the watermass should allow forecasting and mitigation against future disastrous events.

A3.2 DIENG VOLCANO, INDONESIA

The "Dieng Volcanic Complex" encompasses the both the "Dieng" and "Butak Petarangan" volcanoes listed in the Catalogue of Active Volcanoes of the World. The complex consists of two or more stratovolcanoes and numerous small craters and cones of Pleistocene-to-Holocene age and covers an area of 6×14 km on the Dieng plateau in Java. The maximum summit height attained is 2565 m (8,415 feet) at 7.2°S, 109.9°E. Its products range in composition from andesite to rhyodacites (Allard et al., 1989). It forms part of the Suda Volcanic arc of Indonesia which has been active since the mid-to-late Tertiary and is the result of the subduction of the Indian oceanic plate under the continental margin of SE Asia.

Activity in historical times has been restricted to minor phreatic eruptions, sometimes associated with gas emissions, which have caused fatalities. Fatalities occurred during eruptions in 1918 (one killed), 1939 (10 killed), and 1944 (114 killed), 1979 (142 killed) and most recently 1992 (one killed) (Allard et al., 1989; GVN, 1990-; SEAN, 1975-89). The area is volcanologically complex, and the relationships between its numerous and closely spaced volcanic features are uncertain. The complex also represents a significant geothermal prospect, and hydrothermal features such as fumaroles, solfataras, mud pools and hot springs are abundant, defining the extensive fissure system and active eruptive centres. Another typical feature of the complex are sites of persistent emission of almost pure CO_2 (mofettes), especially in the western sector where in places emanations frequently destroy vegetation which the local people refer to as "death valleys".

In February 1979, rapid CO_2 emanations leading to 142 deaths were preceded by a phreatic explosion at Sinila (on the SW portion of the Dieng volcanic complex) which resulted in the formation of a new crater and the reactivation of a pre-existing fracture. CO_2 effusion occurred from both the fracture and the crater, and flowed down to the plain below as a dense sheet (Le Guern et al., 1982). Emanation of CO_2 continued over the next few months at a much reduced flow rate.

It is estimated that the total CO_2 output associated with this eruption may have approached 0.1 km^3 (Allard et al., 1989). The gas emitted was analysed by Le Guern et al. (1982) and found to be almost pure CO_2 (98-99%) with subordinate amounts of CH_4 and S-compounds. Phreatic eruptions by definition, release steam and superheated water with only subordinate amounts of CO_2. Thus an eruption of this type can only lead to effussion of pure CO_2 if this gas is already emplaced in a shallow local reservoir, probably trapped in fractures, pore spaces or aquifers and probably in the form of a high density fluid. The $\delta^{13}C$ of the CO_2 and the He/CO_2 ratio of the gas was found to be almost identical to the nearby Merapi volcano (Allard et al., 1989), and within the range of mantle derived carbon in MOR magmas (Pineau & Javoy, 1983). A magmatic origin is therefore plausible and it is thought that magmatic carbon dioxide had accumulated beneath the Dieng volcanic complex, and its effusion was then triggered by the pressure relase generated by the phreatic eruption. It has also been shown that effusion of concentrated CO_2 occurs frequently within eroded calderas or volcano-tectonic depressions and may account for the major hazard posed by phreatic eruptions within these structures (Allard et al., 1989).

The 1979 event demonstrated that the depressurisation of accumulations of CO_2 at shallow levels beneath volcanoes may represent a major hazard (for local populations) associated with phreatic eruptions, whether it be a trigger or a consequence. The hazard from ongoing CO_2 emanations at Dieng, however persists even between eruptions, as evidenced by the death of four workers at geothermal well in 1988 (SEAN, 1975-89).

Most recently, on 18 March 1992, a sudden gas emission occurred from a fracture close to the 1979 eruption site, which resulted in one death by axphxiation. Surface gas measurements the next day indicated high concentrations of CO_2 and O_2 (40 and 15 weight %, respectively), and lesser concentrations of H_2S and HCN; 200 and 197 ppm, respectively (GVN, 1992).

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