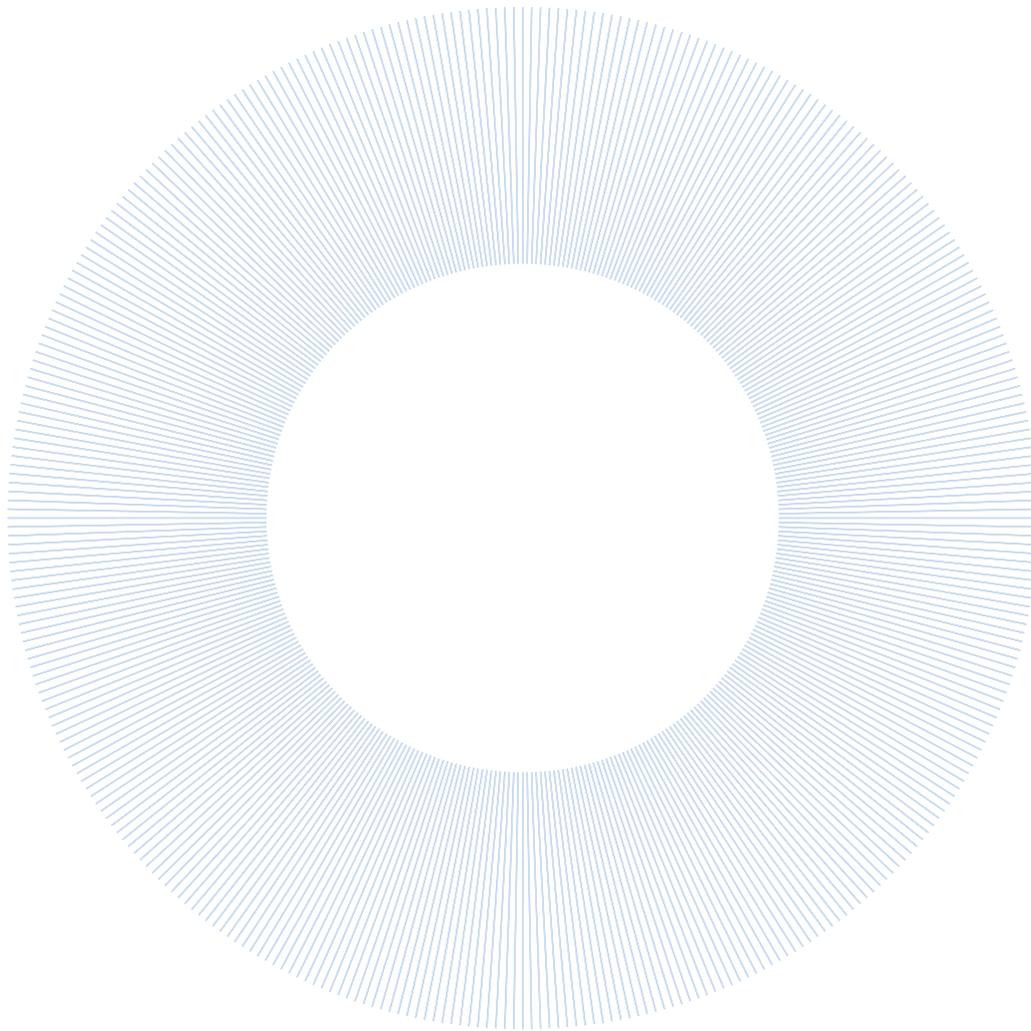


Water and Volcanism



Richard J. Arculus

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WATER AND VOLCANISM

Volcanoes and their eruptions were familiar phenomena to homo sapiens in the species' African development, but among the first recorded speculations, Empedocles identified volcanic activity as a manifestation of fire, one of the four roots responsible for all structures in the world. Impressed by the maritime proximity of many European volcanoes, a belief developed that interaction between the sea and magma is critical in triggering explosive volcanism – nowadays this is termed phreatomagmatic activity. Following the eighteenth-century triumph of the plutonists over the neptunists with respect to the origin of igneous rocks, several nineteenth-century geologists advocated exsolution of H₂O, previously dissolved at depth in the magma rather than via shallow interactions with seawater, as the main driving force for explosions. The enormous expansion accompanying transformation of liquid to gaseous H₂O provides the energy for this explosive activity. We know considerable amounts of H₂O (and other volatile gases such as helium) were accreted during formation of the Earth. Magmas transport these gases towards the surface, and lowered pressure results in exsolution of volatiles.

Igneous petrology and volcanology made little contribution generally to the development of plate tectonic theory, but pioneers such as Arthur Holmes, Harry Hess and Robert Coats were early advocates of crustal recycling, the importance of H₂O in serpentinising the oceanic crust and global recycling of H₂O via subduction zones respectively. Release of H₂O from a subducted plate triggers melting and magma formation in the overlying mantle. Magmas subsequently erupted in arcs developed over subduction zones are much richer in H₂O than at ridge or hot-spot settings. It appears the most important continental crust-building blocks are the basalt-andesite-dacite-rhyolite suites formed in arcs. The bulk composition of the continental crust is known to be equivalent to andesite, and the distinctive trace element geochemical characteristics of the continental crust are only matched by arc magma types. The aphorism 'no water, no granites – no oceans, no continents' summarises the importance of H₂O in global recycling and the genesis of continent-forming arc magmas. Earth seems to be the only planet with plate tectonics and a fundamental question is whether a liquid hydrosphere (unique to Earth among the terrestrial planets) is a necessary condition for this style of tectonism.

In addition to H₂O, other potentially volatile and fluid-mobilised elements and compounds (including ore-forming metals) are transported in supercritical fluids exsolved from arc magmas. Beneath the sea floor, these fluids become mixed with recycled seawater to emerge in hydrothermal vent ('blacksmoker') systems. On large scales, precipitation of metallic sulfides from hydrous fluids in the crust leads to large, mineable Au-Cu-rich ore deposits known as 'porphyry coppers.'

In the past century, the possible scale of explosive eruptions driven primarily by exsolution of H₂O, has become recognised. We can extrapolate from observed small events such as Mt St Helens of the Oregon Cascades, through Taupo in New Zealand (50 km³, 1.8 Ka BP; 500 km³, 26.5 Ka BP), to the Oligocene (30 Ma) 5000 km³ of the Fish Canyon Tuff in Colorado. These large eruptions can have significant environmental effects.

Early Thoughts on the Nature of Explosive Volcanic Activity

Given the number of volcanoes developed in and adjacent to the major rift valleys of central and northern Africa, there can be little doubt that volcanic eruptions were familiar phenomena to *homo sapiens* in the species' African development. It is possible that the earliest preserved representation of an active volcano is a putative town plan, drawn ~7000 BC at Catal Hoyuk in Turkey, with the active volcano Hasan Dag on the horizon. The eruption of Santorini in the Aegean Island Arc in 1620 BC was among the most destructive known; the demise of the Minoan civilisation of Crete has been attributed to the combined effects of earthquakes, ash falls and tsunamis resulting from Santorini.

Among the first recorded speculations, Empedocles (490–430 BC) identified volcanic activity as a manifestation of *fire*, one of the four *roots* responsible for all structures in the world. A variety of Greco-Roman philosophical speculations subsequently emerged on the origins of volcanic activity, none with any persistent merit. Impressed by the maritime proximity of many European volcanoes, a belief developed that interaction between the sea and magma is critical in triggering explosive volcanism – nowadays this is termed *phreatomagmatic* activity. In 1788 AD, for example, Lazzaro Spallanzani visited Vesuvius, the volcanoes of the Lipari islands and Sicily. Noting the presence of several gases in the lavas of these volcanoes, Spallanzani suggested 'water, principally that of the sea' was important in triggering eruptions. Despite the clear field evidence for origins of igneous rocks from formerly molten material called magma, for a while the 'neptunian' hypothesis of A. Gottlieb Werner (1749–1817) found considerable following; neptunists believed all rocks are precipitated from oceans and seas. However, the rival plutonists held the view that some rocks were originally molten. This was originally proposed by the Abbé A-L Moro (1687–1750), further advocated by Nicolas Desmarest (1725–1815) and subsequently by James Hutton (1726–1797).

A major scientific breakthrough in understanding the origins of explosive volcanic eruptions was rooted in the late seventeenth to early eighteenth-century development of thermodynamics and steam engines. Among the systematics of pressure-volume-temperature relationships of gases, liquids and solids, the enormous volume change (~3 orders of magnitude) accompanying the transformation of liquid to gaseous H₂O has particular significance. Rather than driving simple phreatomagmatic explosions, a more profound role for water was suggested. For example, several nineteenth-century geologists including George Scrope (1797–1876), advocated exsolution (i.e. formation of a gas phases in equilibrium with the liquid silicate magma) of gaseous H₂O, previously dissolved at depth in the magma as the main source of energy for explosions. Rather than being a simple near-surface magma-seawater interaction, these geologists were proposing H₂O was already dissolved in the magma at its origins, deep in the Earth. A diagram (Figure 1) from T. G. Bonney (1823–1933) illustrates the concept of ex-solution of H₂O vapour driving an explosive eruption.

Osmond Fisher (1817–1914) suggested H₂O exsolving from magma is primordial in the sense of being trapped within the Earth during the planet's formation. Given the distinctiveness of the D/H of our hydrosphere compared with solar or cometary values, we know the major source (so-called 'planetary') of our oceans was from the Earth's interior via degassing rather than direct accretion from the solar nebula or as a late-stage cometary veneer. Helium is an egregiously chemically inert but potentially volatile element. Together with H, it is the only element or molecule that Earth's gravitational field is incapable of retaining in our atmosphere. Helium has two isotopes: ³He and ⁴He. While the latter is continuously generated in the Earth (as 'α particles') through the many decay steps of U and Th, ³He is not generated

during radioactive decay. Any ^3He now leaking out of the Earth through igneous activity must be primordial – an unknown initial amount was trapped within the Earth 4.567 Ga ago, and has been ‘leaking’ to the exterior and thence into space ever since. Current emission of ^3He accompanying volcanic activity has been mapped extensively at ocean ridges, arcs and backarcs, and hot spots such as Hawaii (e.g. Lupton et al., 2004). The important conclusion is if an extremely volatile element like He was trapped inside the Earth at its birth, then other less volatile elements and compounds such as H_2O , C and CO_2 were inevitably trapped as well. And if some primordially-trapped ^3He is still escaping from the Earth’s interior, then presumably some fraction of the H_2O currently emitted by volcanic activity is also primordial in the same sense.

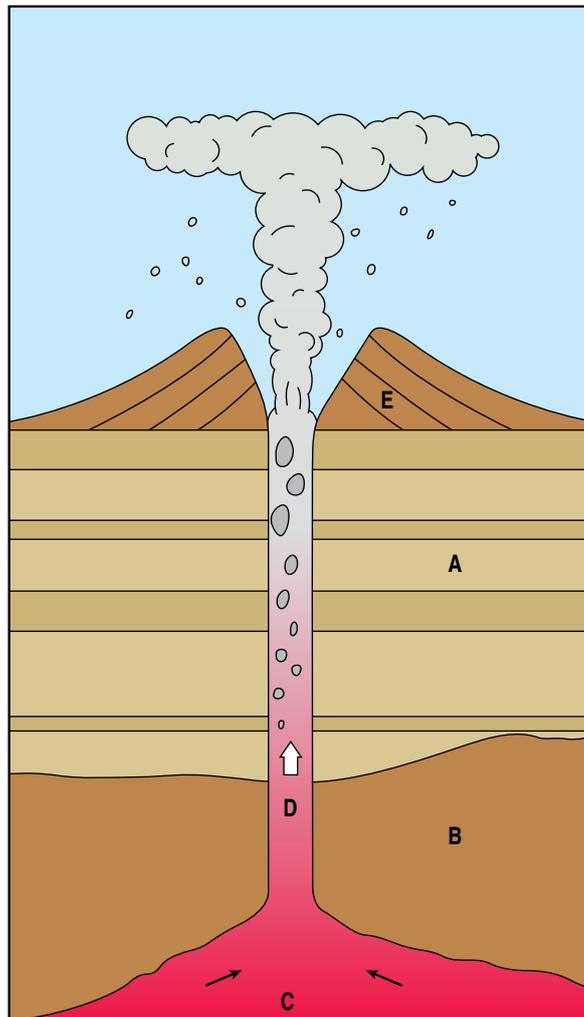


Figure 1: Bonney’s conception of the exsolution and expansion of H_2O vapour from an ascending magma, driving an explosive eruption. A and B are sedimentary and crystalline rocks of the Earth’s crust respectively. C is the magma chamber and D a feeder dyke to the vent. E is the pyroclastic cone and crater.

Volcanological and Petrological Contributions to Plate Tectonics

If geologists had been able to see the floor of the oceans with the kind of detail that modern multi-beam sonar swath mapping is capable of achieving, the plate tectonic paradigm would have emerged a long time before the last 50 years. Studies by European-based scientists of volcanoes and their products were not critically important in the development of this paradigm. The range of volcanism accessible to Europeans was large and to some extent challenges even present understanding. For example, the hot spot of Etna is adjacent to the geographically restricted Aolian Arc which includes Stromboli, the eponymous Vulcano,

and strongly crustally-contaminated Vesuvius. While forays to African volcanoes discovered a plethora of geochemically-distinctive lava types, apart from an obvious association with the topographically prominent rift valleys, no additional globally significant tectonic or geophysical insights were forthcoming.

Arthur Holmes (1890–1965) is an important figure in the context of the development of plate tectonic theory. Holmes was a staff member of the University of Durham from 1924 to 1943. He quickly appreciated and applied the chronometric potential for Earth sciences of the radioactive decay of U to Pb, asserted the existence of mantle convection, and argued the case for continental drift when it was unpopular with most geologists. Holmes was also an igneous petrologist who recognised the geochemical similarity of the bulk composition of the continental crust with the most voluminous outpourings of Andean-type volcanoes ('andesite') and their subjacent plutons.

Harry Hess (1906–1969) had established a scientific reputation for gravity studies in the West Indies island arcs, bathymetric surveys and the discovery of 'guyots' conducted during Navy operations in the western Pacific, expertise in the important pyroxene group of igneous rock-forming minerals and the origin of serpentine (hydrated equivalent of olivine and orthopyroxene). However, his seminal contribution was the proposal in the early 1960s that the Earth's oceanic crust is formed at, and moves laterally away from, mid-ocean ridges (e.g. Hess, 1962). Following the Second World War, burgeoning military requirements for knowledge of bathymetry, magnetic and gravity fields in the oceans drove a huge increase in geomarine exploration. Amidst a wealth of new topographic and magnetic data, identification also in the early 1960s by Lawrence Morley, Fred Vine and Drummond Matthews of welts of crust, oppositely polarised magnetically, and symmetrically-arranged parallel to the mid-ocean ridges, confirmed the sea floor spreading hypothesis; development of the plate tectonic paradigm over the next few years revolutionised the Earth sciences.

'No Water, No Granites – No Oceans, No Continents'

The title of this section is an aphorism coined by S. Ross Taylor and Ian Campbell of the Australian National University (ANU). It succinctly states the intimate connection between the genesis of the most important building block of the continental crust ('andesite') and the presence on Earth of a long-lived hydrosphere (Campbell and Taylor, 1983). We now recognise the vital link between the long-term recycling of H₂O from the exterior of the Earth back into the interior via plate subduction, and the generation of magmas in arcs geographically associated with the sites of subduction – deep sea trenches. An abbreviated history of the development of these concepts is useful.

Arcuate geographic features on the Earth's surface such as the mountain chains of the Alps and Himalayas formed prominent barriers to human migration and logistic limitations on military expansivity. Similarly, along the margins of the Indian and Pacific oceans, the pioneering *homo sapiens* that journeyed out of Africa through the Far East to Australasia, followed in the Pacific by Melanesian and Polynesian explorers, were all most likely well aware of the many arcuate chains of volcanic islands from the point of view of migration routes and colonisation potential.

Geographers and geologists came to appreciate the difference between non-linear archipelagos like the Galápagos with many individually active volcanoes, island chains such as Hawaii (Darwin, 1842), characterised by active volcanism only at a terminal island accompanied by

varying degrees of erosional degradation, including fringing reef and atoll development, with increasing distance from the active locus (e.g. Hawaii), and chains such as those in Indonesia where many of the constituent volcanoes are concurrently or potentially active. Equivalent chains of active volcanoes were also recognised in the cordilleran mountain ranges of the continents, such as the Cascade Range of western North America and the Andes of South America. These latter types are what we now call island and continental arcs respectively.

The origins of the arcuate shapes of many island arcs in the western Pacific attracted scientific attention. For example, Sollas (1903) showed that an arc could be simply the outcrop of a planar fault on the Earth's spherical surface. Lake (1931) subsequently suggested that Asia is being thrust over the crusts of the Pacific and Indian oceans along these fault surfaces, and presciently proposed that the continentward-dipping zones of earthquake foci documented by Wadati in 1931 for Japan marked the trace of these types of thrust.

Plate tectonic theory specifically identified deep-sea trenches as the loci of plate subduction. Among those who appreciated the significance of these processes in terms of transport of materials accumulated on the surface of the oceanic crust during its migration from ridge to trench was Robert Coats (1910–1995). He was involved in the post-Second World War mapping effort by the US Geological Survey of the Aleutian Island Arc. The Aleutians were an early choice for underground nuclear weapon tests, and it was clearly important to know something about the geology of the container. In 1962, Coats published a remarkably insightful paper into the origin of the Aleutian Arc, wherein he linked the dipping zone of seismicity (Wadati-Benioff Zone) to underthrusting of the Pacific Plate, the transport of H₂O and oceanic sediments into the upper mantle, and the melting of these materials, as crucial for the generation of andesites erupted in the Aleutian volcanic arc: the diagram he used to depict these relationships is shown as Figure 2 with his original caption.

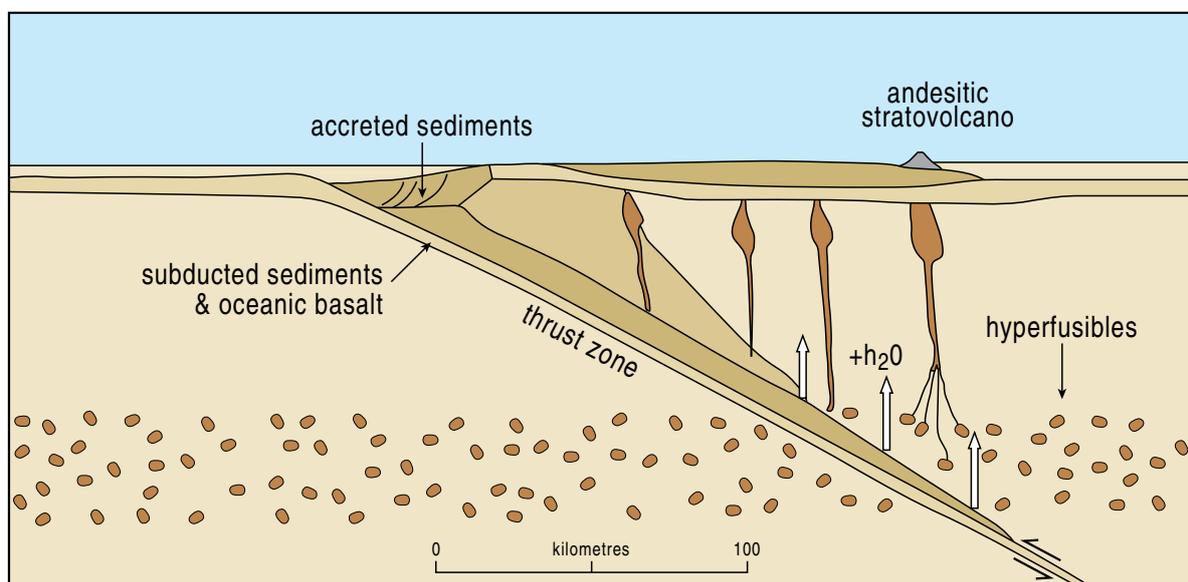


Figure 2: 'Cross section through crust and upper mantle of a generalized island arc, showing suggested mechanism for development of andesitic rocks through addition of water and hyperfusible materials from eugeosynclinal deposits to eruptible basaltic material in the mantle. Steeply dipping tear faults in the upper plate, though probably numerous and important in localizing volcanic centers, have been omitted' (Coats, 1962).

Ross Taylor together with Alan White of the ANU recognised that the distinctive geochemical composition of the continental crust is uniquely matched by that of andesite, the archetypal rock type characteristic of island and continental arcs. Two major observations made were: continental crust has an overall composition equivalent to andesite (SiO₂ wt% ~60);

continental areas grow mainly by the addition of andesites and associated rocks in areas of plate convergence. The main rock types forming the exposed upper continental crust (granodiorites and granites) are predominantly formed by a renewed cycle of melting of andesitic protoliths (Taylor and White, 1965).

H₂O in the Plate Tectonic Cycle

In the past 50 years, through a combination of field work, experimental petrological studies, laboratory analysis and theoretical considerations, we have a firm understanding of the critical role of H₂O in the generation and evolution of island and continental arc magmas. Three major processes are significant: H₂O-rich fluids released through the process of pressure- and temperature-dependent breakdown reactions of the varied lithologies forming the subducted plate selectively transport fluid-mobile elements from the plate into the overlying advecting wedge of mantle between the overriding and downgoing lithospheres; the fluid migrates upward in the wedge triggering partial melting and formation of magma; the fluid is dissolved in the magma, transported surfaceward, and is responsible for marked changes in the crystallisation behaviour of the magma compared with relatively dry equivalents in ridge and hot-spot settings (e.g. Arculus, 2004). We can examine each of these processes in a little more detail.

The subduction regime is unusual for a terrestrial planet because the relatively cold, outer mechanical and compositional boundary layer (lithosphere) is recycled into the mantle. For Earth, the lithosphere is gravitationally unstable with respect to the underlying mantle after cooling and thickening away from a mid-ocean ridge for a few million years. In fact, the major driving force of plate tectonics is 'plate pull' rather than the 'ridge push' accompanying uprising mantle at the mid-ocean ridges. For a subducting oceanic plate, the package of oceanic sediments, hydrated and carbonated igneous oceanic crust and underlying mantle experiences a series of metamorphic changes in response primarily to increases in pressure and secondarily to temperature rise. Dehydration reactions such as those from clays through micas and amphiboles to anhydrous mineral assemblages dominated by pyroxenes and garnet occur. Prior to the development of plate tectonics, metamorphic petrologists had established facies (mineral assemblages characteristic of different pressure-temperature regimes) for a variety of different rock types. Miyashiro (1961) recognised the tectonic significance of 'paired metamorphic belts' in the Japanese arcs where linear zones of rock assemblages characteristic of low temperature-high pressure are located systematically trenchward of high temperature-low pressure belts.

The fluids released from the subducting plate are enriched in elements that are relatively soluble in the fluid compared with those that are insoluble. Geochemists have established the relatively high hydrous fluid solubility of elements such as the alkalis (including K, Rb and Cs), alkaline earths (Sr, Ba), U and Pb. And these elements are dramatically enriched in arc magmas compared with elements of similar overall magma-residual mantle behaviour such as high field strength elements (e.g. Nb, Ta, Zr, Hf) and the higher atomic number lanthanides.

The overall trace element abundance systematics in arcs are unlike those of ridges and hot-spots, and match closely the geochemical composition of the continental crust (e.g. Davidson and Arculus, 2005). In detail, the exact nature of fluids lost from the subducting plate is the subject of active research. It is possible for example, that supercritical behaviour is important. There is, however, general agreement that preferential hydrous fluid mobility is the key phenomenon.

For most of the time and in most places, seismological evidence shows that the Earth's mantle behaves as a plastic solid; locally, two major types of localised partial melting can occur. The first of these melting processes is adiabatic decompression, and the second results from fluxing by a fluid such as that released by a subducting plate. The former process takes place beneath ocean ridges and hot-spots and results from the poor thermal conductivity of silicate mantle, its consequent retention of temperature during decompression through induced upwelling, and the resultant intersection of uprising solid mantle with the less steeply inclined (in pressure-temperature space) melting curve. There is considerably less scope for upwelling of mantle beneath arcs; magma production is most likely dominated by the ingress of subducted plate-derived hydrous fluids, which are known to lower the melting point of the upper mantle by several hundred degrees. In general, 1% of extra partial melting of the mantle takes place for every 0.1wt% added H₂O (Stolper and Newman, 1994). For many intra-oceanic arcs, the total percentage of melting of the mantle source beneath the arc exceeds that of mid-ocean ridges but the total global volume of melt generated in arcs is likely to be ~0.25 of the total mid-ocean ridge volume, presumably because the volume of the mantle source is relatively restricted beneath arcs compared with ridges.

The timescales for migration of H₂O-rich fluids from the subducted plate, through the wedge and erupted at surface have been studied for the past 20 years with the use of radioactive disequilibria between parent and daughter isotopes in the decay chains of U and Th. Astonishingly, it seems that in some cases, ~5000 years is all that is required to accomplish this journey from the moment H₂O is released from the subducted plate to volcanic eruption (Turner et al., 2001).

There are several lines of evidence that arc magmas contain significantly larger amounts of H₂O and other volatile elements and compounds than those associated with mid-ocean ridges and hot-spots, such as Hawaii, Réunion and the Galápagos. The first of these is the explosive character of arc eruptions, as argued by Scrope and Bonney. The second is the presence of hydrous mineral phases, such as amphibole and mica; and finally, geochemical analysis of arc rocks show higher abundances of H₂O than in those of other major tectonic environments. We have found most volatiles are in fact degassed during subaerial eruption; analysis of glasses formed during submarine-quenching of arc magmas whereby a greater proportion of the volatile load is retained, together with glass (formerly melt) inclusions trapped in phenocrysts of these magmas has shown the average H₂O contents of basaltic parental arc magmas are in the range ~2 to 6wt%, one to two orders of magnitude more for example, than in basalts of mid-ocean ridges (Wallace, 2005).

In addition to generating enormous explosive potential for arc magmas, the presence of dissolved H₂O has some profound consequences for other igneous processes. While seemingly of arcane interest only, H₂O crucially alters the crystallisation sequence of the mineral phases that form in the magmas. Overall these phases have two important general characteristics: they are compositionally different than their host magma, unlike the case of ice in pure H₂O; and they usually have a different density than their host magma. Settling or floating of crystals of contrasted individual compositions leads to a process termed fractional crystallisation (e.g. Bowen, 1928), producing a sequence of derivative, generally higher-silica magma types from basaltic (low-silica content) parents. In relatively dry mid-ocean ridge basalts, the typical silicate mineral crystallisation sequence is first olivine, then plagioclase feldspar, followed by clinopyroxene and late orthopyroxene. For relatively wet arc magmas, several important differences are observed. Clinopyroxene precedes plagioclase and once stabilised, the plagioclase is more calcic and less silica-rich than is the case in mid-ocean ridge basalts. In some arcs such as the Lesser Antilles, amphibole is an early crystallising phase, sometimes

even preceding plagioclase. Although the reasons are still not fully understood, another general characteristic of arc magmas is their relatively oxidised nature compared with mid-ocean ridges; this leads to earlier stabilisation in the crystallisation sequence of an important non-silicate mineral: magnetite (Fe_3O_4).

The net effect of these contrasting fractional crystallisation histories is the production of relatively large volumes of alkali element-silica-rich derivative melts such as andesites, dacites, and rhyolites in arcs, and the dearth of such compositions at mid-ocean ridges or hot-spots. The most plausible source of extra H_2O in arc magmas compared with these other volcanic environments is from subducted plates. Among the terrestrial planets, only Earth is known to have plate tectonics and an andesitic continental crust; both may be the result of a long-lived hydrosphere.

Degassing of H_2O and Other Volatiles from Magmas

The solubilities of H_2O , CO_2 , S species (SO_2 and H_2S), and the halogens in a range of magma compositions are reasonably well known through experimental studies over ranges of pressure from near atmospheric to ~ 3 GPa (equivalent to about 100 km depth in the Earth). A representation of the solubility of H_2O in a magma is shown in Figure 3.

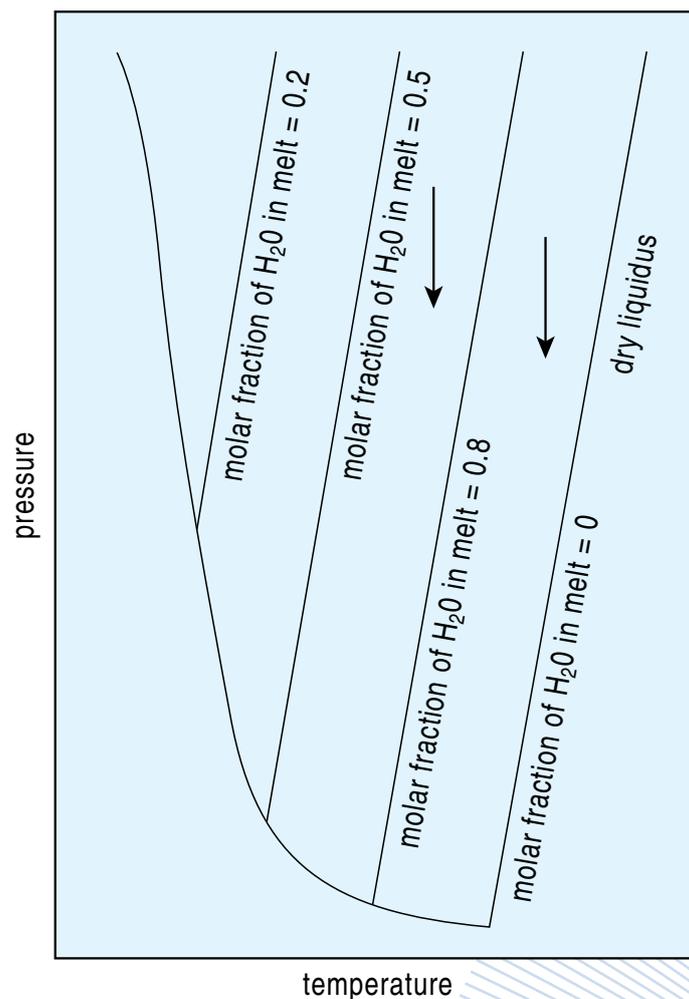


Figure 3: Diagram of the effect of pressure and temperature on the solubility of H_2O in silicate magma. More H_2O is dissolved as a function of increasing pressure, and less with increasing temperature. The dry liquidus defines the boundary between crystal-free melt and crystal bearing melt. The solidus defines the boundary between the presence of melt and all-solid material. The arrows depict representative ascent paths of a magma; depressurisation forces the diminution of H_2O solubility in the magma and degassing results.

The important features are the isothermal increase in solubility of H₂O with increasing pressure, and isobaric decrease of solubility with increasing temperature. Generally on ascent, H₂O will be lost from magmas through saturation with a separate gas phase and escape of gas due to relative buoyancy. Gas phase saturation is initiated by the least soluble volatile species, generally CO₂. All other potentially volatile species are partitioned to greater or lesser extents between the gas and melt phases. Not all of the partitioning relationships are yet well known, particularly for elevated pressures and temperatures. But the net effects noted for erupted arc magmas are extensive loss of CO₂ and the S species, and less pervasive loss of H₂O. In fact, if the magma becomes saturated with a hydrous silicate such as amphibole, a considerable fraction of H₂O may be retained in this crystalline host, a process called an amphibole 'sponge' (Davidson et al., 2007).

A volatile phase escaping from a magma is chemically complex and typically supercritical. At crustal pressures and a few hundred degrees, this phase may itself separate into two new phases: a dense liquid or brine and a gas. These phenomena are of great interest to economic geologists because noble (e.g. Au) and base metals (Cu, Zn, Pb, Mo) are transported from cooling magmas by escaping fluids and gas; these may stall and cool within the upper regions of the crystallised shell of the magma chamber, or fracture and precipitate sulfides in the carapace of surrounding crustal rocks, potentially to form ores such as the immense 'porphyry copper' deposits of the American cordillera and the Andes. The emplacement of magma in the crust also established convective ground water systems; heated meteoric water combines with magma-derived volatiles in the transport and precipitation of sulfides. These processes are depicted in Figure 4.

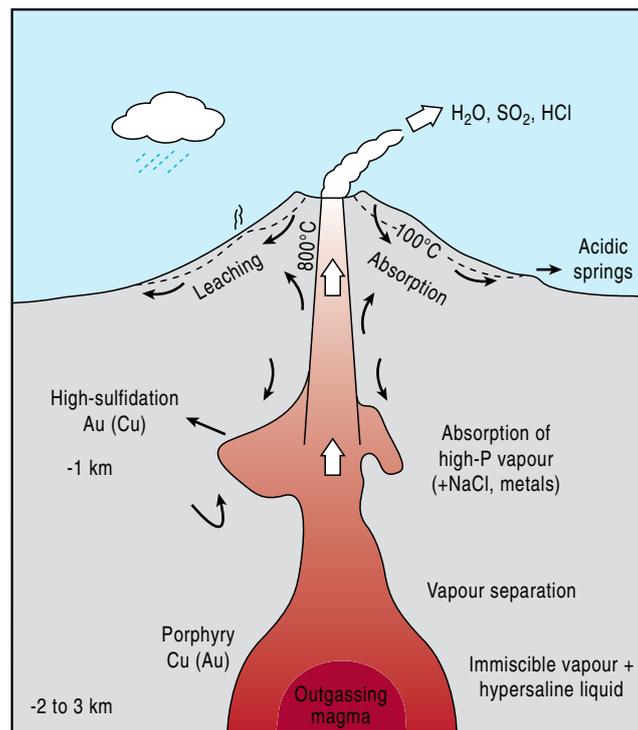


Figure 4: Schematic diagram of magma-derived vapours and fluids and formation of porphyry copper deposits.

The first discovery of so-called 'black smokers' on the ocean floor was made on an oceanic spreading centre in the eastern Pacific about 30 years ago. An explosion of scientific effort has ensued on these submarine hot springs including geochemical, geophysical, hydrological and biological studies. The smoke comprises precipitates of iron oxyhydroxides and metallic sulfides. A convective hydrologic cycle has been determined involving the drawdown of cold

sea water through the oceanic crust, heating due to proximity of a sub-ridge magma chamber, chemical exchange between water and oceanic crust, and buoyant uprise of heated water (up to $\sim 400^{\circ}\text{C}$) to an emission outlet at a smoker chimney or other type of vent. We know that some of the volatile gas species and metals degassed from cooling and fractionating sub-ridge magma chambers are included in the hydrothermal vent emissions. Over the past decade, many more of these hydrothermal vent systems have been discovered on submarine island arc volcanoes (e.g. de Ronde et al., 2003) and adjacent backarc spreading systems in the western Pacific. The high ore grades of the hydrothermal metal sulphide deposits of these particular systems mean that they are potentially mineable, and are current targets of several exploration companies. Collectively, these systems provide about 25% of the total hydrothermal input into the Pacific Ocean.

More on Explosive Eruptions

Several terms describing specific styles of explosive eruption derive from observations of the behaviour of Italian volcanoes. For example, the climactic and intensely explosive eruption in 44AD of Vesuvius was documented by Pliny; a column of ash reaching stratospheric heights ($\sim 10\text{km}$ or more) capped by a mushroom cloud with subsidiary tropospheric layers generated by wind shear, generally with the appearance of a Lebanese cedar tree, is still referred to as a 'plinian' eruption. The terms 'strombolian' and 'vulcanian' refer to styles of less explosive but semi-continuous, low-level explosive activity.

In the past 40 years, we have begun to appreciate the enormous volumes and power of some of the eruptions that have taken place in the past 10^5 years, indubitably witnessed in some cases by *homo sapiens*, and far exceeding the early scientific conceptualisations of Scrope and Bonney. In the nineteenth and twentieth centuries, several relatively small volume, but nonetheless spectacular, explosive arc volcano eruptions occurred, that became scientifically well documented in terms of eye witness accounts and forensic analysis of the eruptive products. These include the 1884 eruption of Krakatau in the Sunda Strait between Java and Sumatra, 1902 eruptions of Mt Pelée and the Soufrière in the Lesser Antilles, 1951 eruption of Mt Lamington in Papua, 1956 eruption of Bezymmiany in Kamchatka and 1980 eruption of Mt St Helens in the Cascades of Washington State. Field studies of thicknesses and grain sizes of the resultant deposits permitted modelling and scaling of the explosive processes to much larger historical and older eruptions (e.g. Sparks, 2003).

For comparative purposes, the decapitating lateral blast of Mt St Helens produced $\sim 3\text{ km}^3$ of pyroclastic material, and that of Krakatau $\sim 25\text{ km}^3$ and a caldera $\sim 4\text{km}$ in diameter. But much larger volumes and more explosive eruptions have been discovered, including: the 1000 km^3 eruption $\sim 80,000$ years ago at Lake Toba (Sumatra), the caldera-forming, $\sim 500\text{km}^3$ Oruanui eruption at Taupo (New Zealand) 26,500 years ago and the $>5,000\text{ km}^3$ 30 million-year-old Fish Canyon Tuff at Creede in Colorado (USA). Large eruptions such as these must have had global climatic effects. Calderas are topographic depressions generated by the exhumation of so much material from crustal magma chambers that the ground collapses post-eruption.

Enormous eruptions pose a number of scientific challenges, including: how does so much magma accumulate in the crust over what time scales, what triggers an eruption, why are they so violently explosive, how long do these huge eruptions last and how much magma remains in the crust? In some cases, a plausible trigger seems to be injection of a new hot pulse of relatively dense basaltic magma at the base of a resident rhyolite-filled chamber of lower density and temperature. Heating of the rhyolite by the underplated basalt can cause

H₂O saturation and lowering of density to the point of buoyant instability. Failure of the magma chamber roof initiates the eruption, which then continues as a runaway because of decompression and further gas evolution. Fragmentation of the magma is a consequence of the failure of the material to keep pace with the rate of gas-driven expansion. Degassing of H₂O results in an increase in magma viscosity which further stiffens the response of the rhyolite magma to rapid strain. On eruption, pyroclastic, pumiceous rhyolite magma blebs can nevertheless be hot enough that welding may occur, resulting in a solid rock body of formerly fragmental pyroclastic material; these sheets are known as 'ignimbrites' or preferably 'welded pyroclast flows.'

Concluding Remarks

Many grand questions concerning the abundance and distribution of H₂O and its role in plate tectonics, the genesis of the continental crust and volcanic activity remain unanswered. While we know the isotopic characteristic of terrestrial H₂O is unlike that of either solar or cometary origin, from whence and when H₂O was accreted in the early Earth is unresolved. On the basis of I-Xe isotopic systematics, it appears that 'catastrophic' degassing of H₂O from the Earth's mantle, presumably by vigorous volcanism, occurred early (within ~100 million years after formation) in the planet's history. How much H₂O remains in the mantle is uncertain but may be equivalent to the total of the external hydrosphere. Cycling of H₂O through the mantle presumably has been continuing since plate tectonics commenced, but timing of the onset and early style of plate tectonics is controversial.

For the present Earth, many uncertainties pertain to the stocks and fluxes of H₂O between the exterior and interior; although we have some ideas of the extent of hydration of the oceanic crust and consequently how much H₂O is subducted each year, the return flux across arc systems remains poorly constrained. In the absence of any return flux, and without accounting for the extent of serpentinisation of the deeper crust and uppermost oceanic mantle through exposure to the seafloor, complete subduction of the external hydrosphere is possible within ~500 million years. Although this is a lengthy time, there is no evidence that ocean volumes have decreased at all through time. Neither, however, is there any reason for the Earth to be in steady state with regard to subducted and returned H₂O fluxes.

Geochemists agree that the ultimate source of the continental crust is the Earth's mantle. While the geochemical fractionations of trace elements observed in active arc systems are characteristic of the continental crust as a whole, what is not so clear is the extent to which modern arc systems are simply recycling continent-crust derived materials, either through dehydration and melting of the superstrate of continent-derived sediments on subducting plates, or via a solution cycle from continent to ocean to ocean crust, subduction, and thence again to arc magmas. Conceptually, we need to separate the on-going production of potentially buoyant feldspar-quartz-rich, continent-forming crust controlled by the critical influence of H₂O on the phase relations of fractionating basaltic magma parents, from the recycling of H₂O-soluble, continent-derived trace elements through subduction zone systems.

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Insights

Insights is edited by Michael O'Neill, IAS Director and Professor of English.
Correspondence should be directed to Audrey Bowron (a.e.bowron@durham.ac.uk).