

Groundwater in fractured rocks

Selected papers from the Groundwater in
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Cover photograph: Outcrop of the weathered granite in the Melechov region, Central Bohemia, Czech Republic. Fractured granite merges upwards into its regolith with granite blocks and a thin soil cover on the top (Photo: Jiří Krásný). Deep parts of the Melechov Granite were selected as one of the places for possible radioactive waste disposal.

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CHAPTER 5

Groundwater in volcanic hard rocks

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ABSTRACT: Volcanics include a large variety of rocks of magmatic origin with a wide range of chemical composition and emplaced on the Earth's surface as molten or partially molten material. Tephra may dominate near explosive volcanoes, while away from the effusion centres, lavas are the main constituents. Dykes play a variable role, from a barrier to groundwater to a water-collecting element. Fresh lava breccias may be one of the most permeable geological formations, while lava cores and welded tuff behave as some of the less permeable materials. Permeability is fracture dominated and tends to decrease with depth, yet there can be noticeable exceptions. Volcanics can be thermally weathered to a low permeability rock by water, especially if CO_2 is plentiful. Volcanic CO_2 diffusing from the deep cooling magma chambers is an important chemical reactant that may produce Na-HCO_3 waters.

1 INTRODUCTION

Volcanics represent a wide variety of rocks and formations that have taken their common origin from different types of magma poured on the Earth's surface. In addition to these effusive rocks, typically lavas and tephra, they include also intrusive formations, linked to volcanism, such as dykes and sills, and also cooled magma chambers, weathering of sediments and rocks derived from volcanic materials, and complex sedimentary bodies directly associated to volcanic activity. Such a variety results in extremely diverse hydrogeological conditions of these rocks.

Large volcanic formations have arisen at continents and islands over the Earth's long history. These range from flood basalts of low viscosity that cover extended areas (Walker, 1980, Macdougall, 1988, Lin and van Keken, 2005), large fissural effusions that can be traced along up to tens of km, to more acid rocks (andesites, rhyolites) that do not form widespread formations but may be large and thick along long strips, as in the western parts of the Americas and in Japan. Rates of eruption may be up to one km^3 of magma per year per volcano and several hundred km^3 per series of events (Swanson et al., 1975; Versey and Singh, 1982). Flood basalts correspond to intense events that can be able to produce enormous, thick plateaus of more than 10^6km^3 in a few thousand years at rates of up to 0.15 m/year (Sen et al., 2006).

The sea floor may be formed by thick volcanic formations, mostly basalts, resting on a densely injected dyke layer covering intrusive gabbro bodies (Wilson et al., 2006). In some cases, these formations now occur on continents or in islands after being tectonically uplifted (e.g., Cyprus).

There are numerous volcanic islands; most of them consist on submarine volcanics topped by subaerial effusions (e.g., archipelagos of Hawaii, the Canaries and Azores; Tahiti, Iceland, Reunion), where they form some of the highest Earth's mountains, up to some thousand metres from bottom to top. On the continents, volcanic materials pile up on older sediments and formations (Etna in Sicily, many of the Andean and Central America high volcanoes).

This paper comments on general geologic properties of volcanics, with a special focus on their hardrock character, to give a background on their main differential hydrogeological characteristics. It utilizes experience gained in diverse projects and his exchange of knowledge with many professionals and experts, not directly cited herein but to whom the author credits much information. This report addresses volcanic rock hydrogeology in a broad sense but emphasizes the Canary Islands, which represent a varied and extraordinary example of volcanic rock formations in which difficult water supply circumstances has lead to extensive drilling and tunnelling to develop groundwater.

Specific publications on volcanic rock hydrogeology are scarce and fragmental. What was presented in the UNESCO-PNUD sponsored meeting in Lanzarote Island in 1975 is summarized in Custodio (1978; 1987). The UNESCO publication on small islands (Falkland and Custodio, 1991) contains numerous references and comments on volcanic islands. Summary chapters and sections on the topic can be found in some classical textbooks (Davis and De Wiest, 1966; Freeze and Cherry, 1979; Walton, 1970; Custodio and Llamas, 1976; Kovalevsky et al., 2004). General information is not repeated here. Only specific aspects relevant to the understanding of the uniqueness of volcanic rock hydrogeology are analysed.

Regional reports are scarce and most of them include volcanics as one of the existing formations. Good references to the United States are in Back et al. (1988) and just to Central America can be found in Losilla et al. (2001), Krásný (1996) and Krásný and Hecht (1998). References to other parts of the world can be found in the different volumes on groundwater published by the United Nations in the 1980's under the guidance of R. Dijon (UN, 1979-1988). Very detailed studies have been carried out in the Yucca Mountains ignimbrites of Nevada, to evaluate the conditions for high-level radioactive waste disposal (e.g., Bodvarsson and Robinson, 2003).

2 VOLCANIC ROCKS: GENETIC ASPECTS OF HYDROGEOLOGICAL RELEVANCE

Magmas may arise from the deep Earth's mantle in convecting hot spots, the upper mantle along rift zones, or crustal material melting when pushed down at great depths due to the tectonic plate convergence along subduction areas. Magmas are complex mixtures formed by a liquid fraction laden with a crystalizing mass containing solids that may be partially separated by gravity to produce geochemical fractionation. The residual liquid may be progressively enriched in incompatible elements. The incorporation of sediments into the magma may increase the water and CO₂ content and may produce less warm, more viscous, explosive magmas near the land surface.

A wide variety of magmas and volcanic formations can be expected, even if coetaneous. Each volcanic formation is unique, although broad classes can be defined: hot-spot volcanism (Hawaii islands, the Canaries, Azores, Etna), plate ridge volcanism (Iceland, Kilimandjaro,

submarine mid ocean ridges) and island-arc volcanism (Aegean islands, Japan, Java, the Andes, the Rocky Mountains, the two Sierra Madre in Mexico and California, Central America). Large flood basalts are probably due to hot-spot volcanism. Island arc volcanism is more prone to produce viscous lavas and large quantities of tephra.

There is a wide range of emplacement modes from the calmed pouring of molten rock (lavas) to highly explosive events that mostly produce fragments (pyroclasts or tephra) thrown into the air or into the water. Viscosity of the molten material and dissolved gas content (mostly water and carbon dioxide) play a key role in the eruption behaviour. Gases are released as pressure decreases. Their escape may be calm, producing scarce lava fragments, or may produce episodic violent explosions in high viscosity, almost solid effusions, in which most of the magma is fragmented and thrown away. Fragments (tephra) may vary from blocks and coarse pyroclasts, that remain and pile up close to the emission point, down to very fine dust particles that may be distributed over very large areas and even the whole Earth (Bindeman, 2006). The sudden and fast expansion of gas-rich magma may produce a fluidized, hot mass formed by gas, dust and particles that is able to flow on the land like lavas of very low viscosity and may cover large surface areas with tuff deposits (ash flows or ignimbrites). Ignimbrites may be intensively or partly welded due to the hot conditions during deposition, or remain more or less loose, with abundant vitreous particulate material. When ash-sized material cools before being deposited they form ash fall tuff, which is primarily nonwelded.

Volcanic formations can be thin layers on the Earth surface that may be later incorporated on into sediments, or up to hundreds and even thousands of metres thick. In volcanic islands there is a large piling of submarine volcanics, topped by subaerial formations that contain lava flows and water-quenched fragmental material (hyaloclastites or aquagene tuff). They can be observed in areas with large upward vertical crustal movements, as in Troodos Mountains, Cyprus (Boronina et al., 2003).

The extrusion of large magma volumes may be accompanied by subsidence if deep magma is not replaced; collapse calderas may be produced. The subsiding or collapsed areas and erosion gullies may be later on filled by reactivated effusions of magma and derived sediments. The ascending magma produces intrusive bodies and a dense swarm of dykes corresponding to the volcanoes' feeders. These often concentrate along the rings limiting collapse calderas or defined rift zones. In hot-spot volcanoes rifting may be radial with 3 or 4 branches.

Near the effusion centers, the structure of volcanic bodies is complex. Vertical dykes are abundant, and also large horizontal dykes (sills) may be found. Where formations are influenced by hot fluids derived from the magma, local rocks, including former volcanics, may be deeply altered and their properties intensively changed. Thermal convection of hot fluids may deeply alter the rock mass. With increasing distance from the effusion centers, complexity decreases in general and materials change into a less heterogeneous piling of lava flows or ignimbrites in which fall fragments proportion decreases, dykes are less frequent or absent, and the alteration effect of deep hot gases is small or nil.

Volcanic formations may be extended in the flow direction but laterally limited. In areas of slow flow or lava ponding a central core of dense but sometimes vesicular rock is typically found with cooling joints and top and bottom brecciated zones due to cooling and drag (at the bottom), with vesicles of gas, especially near the top. The upper part may be smooth or reduced to a thin layer of breccia (pahoehoe lavas), but other times it may be highly brecciated (aa lavas), especially near the lava front. In warm humid climates, weathering

produces a lateritic cover. This is common in India (Uhl and Joshi, 1986) and Brazil, but in the Canaries and Madeira and also in Andean and Central America, chemical leaching is not enough and dark-brown, iron oxy-hydroxide and kaolinite-illite rich soils typically occur (Tejedor Salguero et al., 1985; Van der Weijden and Pacheco, 2003; Deutsch et al., 1982).

Occasionally a lava flow may keep a hot, partly degassed fluid core after the external part solidifies. A sudden rupture of the crust allows the fast emptying of the molten lava core to form a new lava flow, leaving a tunnel that may partly stand for some time. These are mostly ephemeral features since they collapse soon. These "lava tubes", as well as other features such as cavities created by overtopping slabs of solid lava crusts or burned tree trunks have being compared to caves in karst. However, they have no similarity to karstic features, and certainly they do not behave like them; these local heterogeneities lack a network of conduits. They are often dry, although they may concentrate groundwater flow and discharge under suitable, humid conditions.

3 GROUNDWATER FLOW IN VOLCANIC HARD ROCKS

From a hydrogeological point of view, in most cases volcanic rocks are a heterogeneous and anisotropic environment. They possess significant porosity except for some vitreous and densely welded formations. Volcanics can be modelled as more or less permeable blocks separated by a network of conductive features such as fractures, coarse layers, and even sedimentary interlayers. The result may vary from a formation dominated by fracture permeability, as in dense lavas or densely welded ignimbrites, to porous-like formations as in fresh, coarse ash-fall formations (Smyth and Sharp 2006). In large enough volumes, volcanics may approach the behaviour of a continuous, anisotropic, relatively high porosity medium. In some volcanic formations, stratification may be conspicuous with changing thickness and preferential orientation according to the flow direction. The result is a macroscopic permeability anisotropy that in detail depends on features such as open fractures, breccia layers, interflow sediments, dykes, and faulting effects.

The simple Jacob logarithmic method is the most commonly used interpretation tool for pumping tests with reasonable results for heterogeneous formations (Meier et al., 1998; Sánchez-Vila et al., 1999), combined with corrections for well capacity in case of large diameter wells (Cabrera et al., 2001; Sammel, 1974). Upscaling hydraulic properties to the volcanic formation cannot be done directly nor can they be downscaled to a given formation. Detailed scale permeability may vary by more than 7 orders of magnitude from one of the lowest known (densely welded ignimbrites) to one of the highest (recent lava flow breccias). Both porosity and permeability may be greatly changed by rock fracturing and especially by alteration. Alteration tend to smooth variations and to dramatically decrease hydraulic conductivity in zones that have been subject to hydrothermal fluids and magma injections.

The role of dykes ranges from low-permeability barriers to horizontal groundwater flow to a highly permeable features. This depends upon the characteristics of the wall rock, the importance of fracturing (van Everdingen, 1995), and the degree of mineral infilling of the associated fractures (Boonstra and Boehmer, 1986).

A compilation of data on hydraulic properties of volcanic hard rocks is not presented here, but some typical examples are instructive.

The Deccan traps of Western India are one of the extensively studied areas (Athavale et al., 1983; Deolankar, 1980). Regional transmissivity is about $3 \text{ m}^2/\text{day}$ but may locally

be to 15 m²/day, and up to 500 m²/day in exceptional cases for blocky and broken lava (Versey and Singh, 1982). Best conditions for flow are found in some of the vesicular and weathered layers separating the different lava flows. Boreholes often penetrate up to 10 lava flows and only 1 out of 6 interlayers yield exploitable water. Although productivity generally decreases with depth, good conditions are found deeper than 60 m (Uhl, 1979). Secondary fracturing seems to play a role in increasing transmissivity since dry wells are less frequent in valley bottoms than in flat uplands.

The younger (Pliocene–Pliocene) but similar to Deccan traps volcanics the north-western USA are an order of magnitude more productive. The widespread formations like the Paraná (Serra Geral) basalts in eastern part of South America behave as an aquitard with respect the underlying Botucatu sandstone formation of the Guaraní aquifer (Sarres Pessôa, 1982), but still is able to sustain flows averaging 2 L/s, sometimes decreasing to less than 0.6 L/s.

Large acidic volcanics are found along the Mexican transvolcanic belt with deep layers affected by brittle tectonics. Transmissivity may vary between 200 and 800 m²/day for andesites with permeabilities of 0.03 to 1.0 m/day for unfractured and 0.8 to 40 m/day for fractured rocks (Carreón–Freyre et al., 2005).

Ignimbrites tend to be clearly less permeable volcanics. Data from boreholes in Yucca Mountain, Nevada (Hinds et al., 1999) show permeability values of 10⁻³ to 10⁻⁷ m/day that increase to 10⁻⁵ to 10⁻⁷ m/day for welded tuff. But fracturing greatly increases these values when considered at the massif scale.

In Central America extensive and varied volcanic formations are found, mostly from Tertiary to Recent (Losilla et al., 2001, Krásný 1996, Krásný and Hecht, 1998). They vary from basalts to andesites and even to rhyolites associated with large pyroclastic material deposits, both ash-fall and ash-flow, and frequent associated flows (lahars) and alluvium. They are up to several hundred metres thick. Permeability is primarily high in recent volcanics and decreases with depth. Transmissivity values can range up to 5000 m²/day but vary areally and may be less than 50 m²/day. The best conditions for water yield seem to be in thick, saturated, recent fall pyroclasts, but also recent lavas with brecciated tops.

Similar conditions are found in volcanic islands. Young volcanics may be highly permeable, as in the Hawaii islands: a flowing well yielded 180 L/s in confined young basalts in coastal Oahu, and water galleries 320 L/s in Maui and up to 200 L/s in Oahu. In Madeira Island some galleries (levadas) yield more than 100 L/s and some of them are used to produce hydroelectricity. In Tenerife (Canarian archipelago) one of the numerous water galleries produced 150 L/s after being extended. In Lanzarote island (Canarian archipelago) coastal recent volcanics allow pumping 500 L/s with a drawdown of some decimetres.

Pyroclastic material, except for very young to sub-recent deposits, is generally less permeable than young brecciated lavas.

Older, altered volcanics, unearched by erosion, are generally of low to very low permeability, especially when they are thermally altered. Generally little is known about their hydraulic characteristics because commonly they are in high, steep, sparsely inhabited areas and in humid environments, except in the Canaries. The springs in them reflect the discharge of younger volcanics on the top of the fractured upper part of them, as in Hawaii and Reunion. In the densely populated Canary Islands (especially Gran Canaria, Tenerife and La Palma) deep exploration by means of galleries, deep shafts and boreholes, with thousands of km of penetration, allow a detailed observation of deep volcanic rocks. Permeability, although small, is still noticeable at 1000 m below land surface. Examples of

Table 1. Permeability values of volcanics in the Canary Islands.

Island	Formation	m/day
Tenerife (1)	Miocene (old) basalts	
	– close to the structural axis	0.02
	– far from the structural axis	
	* deep seated	0.02
	* shallow	0.05
	Plio-Quaternary (modern) basalt	
– in general	0.75	
– shallow, in some areas	2	
Gran Canaria (2)	Extracaldera, Miocene (old) basalts	
	– “a-a” type	0.01–0.04
	– “pahoe-hoe” type	0.1–1
	Trachy-syenites and trachytes	0.01–0.04
	Phonolites and ignimbrites	0.06–0.09
	Phonolites of Telde area	0.1–0.2 (up to 5)
	Phonolites of Amurga massif (selected wells)	0.5–5
	Caldera-rim materials	<0.002
	“Roque Nublo” volcanic conglomerates	0.15–0.45
	Plio-Quaternary (recent) basalts, Telde area	25 (up to 100)
Quaternary (young) basalts	>1	
Lanzarote (3)	Famara massif Miocene basalts	0.05–0.02

(1) Modified from Custodio (1985). Adjusted by means of a numerical model

(2) Modified from Custodio (1985), Cabrera et al. (2001), Cabrera and Custodio (2003)

(3) Modified from Custodio (1985)

permeability values for volcanic materials in the Canarian archipelago are given in Table 1 to show a wide range of volcanic materials in this area.

Permeability of ophiolite complexes and crustal basalts is low, but it may be greatly changed by fracturing. About one third of the boreholes in old pillow lavas, sheeted dykes and gabbros are successful to yield water in Cyprus (Boronina et al., 2003), especially in the surroundings of fracture zones. Macroscopic porosity is about $5 \pm 1\%$ but varies from about $1.5 \pm 0.5\%$ for flows to $27 \pm 3\%$ for pillow lavas, or reaches $15 \pm 2\%$ if they belong to altered zone close to the sea bottom (Gillis and Sapp, 1977). Densely dyke-injected rocks properties are quite different from the original rock and may approach that of a densely fractured rock. Cold freshwater permeability of basaltic oceanic crust may be 10^{-9} to 10^{-4} m/day for the core of lava flows, and 10^{-5} to 1 m/day as determined by hydraulic tests in boreholes (Fisher, 1998; Manning and Ingebritsen, 1999) but can reach 10^{-3} to 100 m/day in highly fractured zones.

4 HYDROGEOLOGICAL IMPORTANCE OF VOLCANIC ROCK ARRANGEMENT

Properties of volcanic rocks vary with their position relative to the emission point or line. Distal formations tend to be free of pyroclasts and dykes, and are dominated by successions

of lava flows with top and bottom breccias and intercalated sediments, fine ashes, and soils that may control groundwater flow. This occurs in large areas of flood basalts and at the periphery of large basaltic shield volcanoes and results in stratification of various hydrogeological bodies: aquifers and aquitards. Permeability typically decreases with depth due to alteration and compaction of scoriaceous layers.

Close to volcanic vents and outflow fissures structure becomes more complex due to the abundance of pyroclastic material that may dominate in zones of explosive volcanism. Viscous acidic lavas tend to form mounds and thick bodies, yet in many cases they became ignimbrites that may cover large areas and be very thick. They may show a regular stratigraphy, broken by faults, as in the Yucca Mountain, Nevada. In the eruption areas increased presence of dykes, intrusions, and thermally altered materials can be followed. This is often the area of highest original elevation and, consequently, is often subject to intense erosion. The permeability is variable, from relatively high in lavas and young pyroclastic deposits to low and even very low in thermally metamorphosed rocks.

The above also applies to volcanic islands. When these volcanic islands are the result of a hot spot a submarine mound is constructed, which often represents the largest part of the magmatic material, and forms a large shield volcano that finally may appear at the sea surface (Hildenbrand et al., 2005). Magma chemistry evolves from basalts to more acidic forms due to magma fractionation and contamination by crustal materials. Volcanic episodes become more violent, form abundant brecciated deposits and eventually large collapse calderas. Materials close to vents are highly altered by thermal and hydrothermal processes. The caldera collapse and large-scale landslides may trigger a reactivation of volcanic events with the formation of a second shield on the old one and the deposits may fill the caldera and even cover it. Around the caldera rim there is thermal metamorphism. This ends the eruptive period if new magma from the deep mantle is not added, and erosion progressively dismantles the island. Relatively minor volcanic events fed by remaining deep molten magma pockets may follow, although the results may still be spectacular by human standards, and of hydrogeological significance, as the six years of continuous activity in the "extinguished" Lanzarote Island (Canary Islands) in the 18th Century.

The hot spot may be more or less geographically stable with successive large events in the same place, or change its relative position when the Earth's tectonic plates move. In this case the successive supply of deep magma starts a new shield volcano at some distance. This is a well-known situation in Hawaii, Society, and Canarian archipelagos with old (drowned or uplifted) islands on one side and young islands on the other. Oahu is older than Hawaii, Reunion is older than Mauritius, and Lanzarote, Fuerteventura and Gran Canaria are older than La Palma and El Hierro. This migration can also be evident on a given island as in Reunion (Pic des Neiges relative to Piton de La Fourneuse) and La Palma (Cumbre Vieja relative to Cumbre Nueva). This has hydrogeological implications. The erosion of the older parts may expose the "core".

Vertical movements due to magmatism and local tectonics can also be important. In Hawaii Island subaerial volcanics were found down to 1800 m deep (García and Davis, 2001) or close to 1000 m in Lanzarote (Canary Islands), while in Fuerteventura and in Cyprus submarine lavas and oceanic crust crop out.

Often, in volcanic islands there is a core of low permeability volcanics consisting of the thermally-altered parts containing dykes and intrusions with possible shallow volcanic chambers, where the emission of volcanic gases from the cooling and consolidating deep magma chambers may continue. Surrounding the central core there is an apron of lava

flows and ignimbrites that may include landslides and laharic deposits, which constitute the largest surface area and may contain quite permeable materials. This pattern is what appears in the Canary Islands but also in the Hawaiian Islands, even if the interpretation given by some authors (see Liu et al., 1983) differentiates between basal aquifers (in the apron) and dyke-impounded aquifers (in the core). Actually there is only one volcanic groundwater body with largely contrasting permeabilities. In the apron, the water table (piezometric surface) is typically close to the land surface and with a small hydraulic gradient. In coastal areas saline waters can underlie fresh-water bodies even if the latter are confined below recent coastal and offshore sediments, as in Pearl Harbor, Oahu. Low permeability in the core produces very high hydraulic gradients, especially if recharge is high. This creates springs in the valley bottoms and at the foot of cliffs. High elevation, perched springs may occur due to high recharge on local, low permeable heterogeneities. This also happens in continental basalts such as the Columbia Plateau. However, many of these springs are probably outflows from the high main groundwater body in the core through permeable layers or fissured upper part.

When volcanics overlay other pre-existing formations as in the case of the Etna in Sicily (D'Alessandro et al., 2004), the bedrock may play the role of the low permeability "core" or, on the other hand, behave as a drain, depending on relative hydrogeological properties. Thus, volcanics can behave as conductive and storage units or just as recharge collectors.

Along the coast freshwater-saltwater relationships follow common behaviour in other coastal areas (Custodio and Llamas, 1976; Custodio and Bruggeman, 1985). The coastal platform is often steep in volcanic islands, and the materials there are transmissive, recent ones. This means an inland penetrating seawater wedge and a floating layer of freshwater with a mixing zone from thin to thick (Thomas et al., 1996), depending on groundwater flow, heterogeneity, recharge fluctuations, and tidal effects. Vertical changes in volcanics and sedimentary formations that may develop there may produce conditions for confined flow, as is well known in Pearl Harbor, Oahu, Hawaii islands. When the core area is at the coast, the floating freshwater body on sea water is less developed as happens in the Canarian and Cape Verde islands and also in the older of the Hawaiian islands (Izuka and Gingerich, 2003). The extent, nature and elevation of the core relative to mean sea level and the apron play a key role in explaining the conspicuous differences among the different volcanic islands. Along the coastal areas there is often a thin layer of ground freshwater that becomes easily contaminated by marine water from below, as in Easter Island, Chile (Herrera et al., 2004).

Real situations in basalt-dominated islands are often more complex due to the existence of different volcanic centres and/or rift zones, of the same or different age (tree main volcanoes in Hawaii island, the north and south volcanoes of Reunion and La Palma islands) or recent volcanic stages covering older, deeply eroded previous ones (Gran Canaria and Tenerife islands). The core may include volcanic calderas, partly or totally filled with permeable lavas, as in Piton de la Fourneuse (Reunion), Las Cañadas (Tenerife), or the intracaldera formations of Gran Canaria. The flow pattern may be changed by large landslides that are common in high islands (Carracedo 1999; Carracedo and Tilling, 2003). Groundwater in the core area is subject to high hydraulic gradients and important vertical head components. The deep submarine volcanics of many islands are of low but not nil permeability. They may still contain permeable features, as found in Hawaii (De Paolo et al., 2001). The general behaviour is little known.

5 GROUNDWATER RECHARGE IN VOLCANIC ROCKS

Groundwater recharge conditions in volcanic formations are not unique and can be compared with other formations (see Simmers, 1997) and depend on climate, soil, and landscape. In the bare or slightly vegetated land of recent volcanics, infiltration of rain and snow melt can be important, although when very permeable there is enhanced air convection that increase evaporative losses. In low permeability volcanics fracturing and faulting may play an important enhancing role, especially if they are covered by a cap rock able to store water.

Groundwater flow in the unsaturated zone is partly through fractures, and the space and time distribution may be quite complex (Faybishenko et al., 1991). How water penetrates is important, at least in the upper part of the unsaturated zone, where inflow may concentrate in fractures. Fractures become active for conducting water when inflow to them (e.g., from the surface or from the top soil) is greater than the inhibition capacity of the walls. This capacity is very low when the matrix is almost impermeable or is close to saturation. Otherwise most of the recharge flow is through the rock matrix. This is what seems to happen in volcanic rocks in many cases. Very detailed studies have been carried out in Nevada, in the arid Yucca Mountain (Fridrich et al., 1994; Wu et al., 2002; Finsterle et al., 2002; Flint et al., 2001; Sonnenthal and Bodvarsson, 1999; Bodvarsson et al., 2003) to study the feasibility of constructing a deep nuclear waste repository in the thick unsaturated zone of Miocene, densely fractured ignimbrites which are formed by a sequence of welded and non-welded ash-flow layers. Some faults with offsets from 10 metres to some hundred metres go across the whole formation and have a decisive influence in the unsaturated zone water movement. They may be barriers or conductive features, depending on the circumstances. The formations of limited extent, perched saturated levels on top of low permeability vitreous layers favour the down-flow through fault planes in wet periods. Faults are conductive when they cross welded tuff, but not in the non-welded parts (Hinds et al., 1999).

6 SPECIFIC HYDROGEOCHEMICAL ISSUES

General principles of hydrogeochemistry and environmental isotopes in volcanic hard rock are the same applicable to other formations (Appelo and Postma, 1993; Custodio and Llamas, 1976; Mazor, 1991; Mook 2001). The high relief of many volcanic areas favours intense erosion resulting in outcrops of fresh rock. Altitude-dependent isotope changes can often be followed there (Scholl et al., 1996; Custodio and Custodio, 2001).

Yet, volcanic rocks are often more chemically reactive than other hard rocks because of the presence of fine particles, large specific surfaces, and abundance of vitreous matter. Generally volcanic rocks change conspicuously with age for the most compact rocks when they have not been subject to high temperature environmental conditions. Groundwater flow enhances the weathering rate, which is faster the higher the temperature is. Rock weathering may be important in a few years in wet, tropical climate, especially for calcalkaline rocks.

Groundwater in volcanic rocks has typically a low content of chloride, sulphate, and other solutes, even if of marine origin. Chloride can be used to calculate recharge if rainfall contribution is known (Gasparini et al., 1990; Custodio, 1992; Alcalá, 2006). However, old marine water may be trapped in raised low permeability formations (Herrera and Custodio, 2002) or some chloride may be contributed in areas receiving deep warm gases.

High temperature alteration in zones subject to convective hot fluids produce new minerals and voids, and fractures may be totally or partially filled. Water and carbon dioxide, as well as other components, play a dominant role in these changes. Under low temperature conditions clay minerals are formed, especially if CO_2 from deep formations or from decaying vegetation help in lowering the otherwise high pH of water. Smectite is formed, or kaolinite if CO_2 availability is high. The rock frees Na^+ that mostly dissolves in the water, and part of the K^+ and Mg^{++} , depending on the type of clay that is formed. Na-HCO_3 waters are often found. Ca^{++} may pass to the water or be precipitated as carbonate if pH is high, thus filling voids and fractures, and forming duricrusts (caliches) near the surface in dry climates, as in many dry areas of the Canarian and Cape Verde archipelagos.

Submarine volcanics may have trapped marine sulphate after being reduced and precipitated as pyrite. Also they may contain sulphate and sulphur from disproportionation of volcanic SO_2 (Embley, 2006). When subjected to subaerial weathering they release relatively high concentrations of SO_4 .

Acid volcanism from very evolved residual magmas may concentrate incompatible heavy elements. When they are incorporated into the magma, they can be widely dispersed as part of the ash fall during the frequent highly explosive events of such type of volcanism. This may explain the association of rapidly weathered glassy ashes incorporated in sediments, producing poor groundwater quality, since ashes may be able to release relatively high concentrations of As and V, as it happens in large areas of the plains (pampas) of Argentina, or of F.

Except for the small quantities of trapped CO_2 in voids, volcanic rocks are carbon free, so they do contribute little to dissolved carbon. Thus, the recharge ^{13}C and ^{14}C contents are not affected. However, in areas with high flow of endogenic CO_2 or sluggish groundwater flow this volcanic carbon may influence C isotopic values, and ^{14}C dating and interpretation of ^{13}C values may be difficult, even more if calcite is present in fracture infilling. This may be a serious handicap for dating long turnover groundwater reservoirs. For short turnover cases, tritium has been a good tool, and probably will be ^{85}Kr , CFC_3 and SF_6 , but existing experience is limited.

7 CONCLUSIONS

Volcanics are partly hard rocks in which hydrogeological behaviour ranges from a typical fractured hard rock to a heterogenous anisotropic close-to-porous rock, depending on the genesis, degree of alteration, dyke density, effect of magmatic intrusions, presence of palaeosoils and intercalated sediments, and other features. They can form thick sequences of volcanic sediments that may preserve primary and secondary porosity and permeable features at great depth. This helps in producing potentially thick 3-D regional groundwater flow systems.

There can be large differences in mean (prevailing) regional permeability between volcanics far from and close to effusion centres. In the effusion centres low permeability material may dominate, especially if erosion has exhumed the more altered, deeper parts. This means high piezometric gradients and in wet areas the existence of high elevation springs from the unsaturated zone.

General hydrogeological, hydrogeochemical and isotopic principles apply with the specificity of the often high relief and intense erosive effects, and the high chemical reactivity

of volcanics if leaching is intense and the supply of soil CO₂ is abundant. In some areas deep-originated CO₂ may play an important role. Na-HCO₃ waters are frequently found.

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