Chapter 1

SEG Distinguished Lecture
Magma Degassing and Mineral Deposition in Hydrothermal Systems along Convergent Plate Boundaries*

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Introduction
To be honest, I am surprised to find myself addressing a meeting of the Society of Economic Geologists—being neither a geologist nor economic. And looking at the title of my paper, I wouldn’t be offended if people told me that I may be going to talk about something I know nothing about. After listening to some of this afternoon’s talks, however, it is clear to me that I wouldn’t be the only one. With this I don’t mean that the previous speakers were inept but that there are still quite a few basic problems which have to be solved before we may safely say, we know what’s going on in hydrothermal systems. And by basic, I mean basic.

The title of my talk links two processes: magma degassing, something I have been studying now, from the gases’ point of view, for more than 20 years, and mineral deposition, something I had my nose rubbed into by living in close vicinity to some of the biggest gold freaks like Kevin Brown, Jeff Hedenquist, Dick Henley, and Terry Seward. I myself had, quite early on, declared gold a four letter word and had vowed never to use it in any of my papers, together with other uncouthies, such as zinc or lead. Now that the above have dispersed, each into his corner of the globe, I think myself free to reconsider my earlier pledge.

When I joined the now defunct DSIR in 1968, I think it was in the middle of the “neptunistic” period of interpreting processes in hydrothermal systems.

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On the basis of isotopic measurements, Craig (1963) had suggested that by far the major proportions of water in hydrothermal discharges are of local meteoric origin, Jim Ellis and Tony Mahon (1964) had found that most of the chemical constituents of geothermal waters could readily be leached from igneous and sedimentary rocks. In other words, people put on a somewhat bemused look should one invoke a “magmatic” origin of some of the things one found in one’s samples.

Within a few years of arriving in New Zealand I became involved with the chemical surveillance of two of the most active volcanoes there: White Island and Mount Ruapehu. Now these were beyond doubt systems closely associated with magmatic activity, people had “seen and felt” it. The waters produced there were, of course, quite different from those encountered at the geothermal systems and one was allowed, at least tentatively, to consider a magmatic origin of some of the constituents. After several years of observation, it became apparent that White Island went through cycles. Following a high-temperature period in the early seventies, most of the fumaroles cooled down and the earlier, typically volcanic discharges, characterized by gases with SO₂ as the major S-containing species, with lots of HCl, and very little CH₄, slowly reverted to “geothermal” discharges with H₂S as the major S species, very low HCl, and much more CH₄ (Giggenbach, 1987). If such a transition could take place in a bona fide magmatic system, why shouldn’t it also happen at other, less obviously “magmatic” systems? Anyway, White Island started to convince me that magmatic contributions to “geothermal” discharges may be much
more important than generally assumed. By comparing the chemical and isotopic compositions of volcanic with geothermal discharges, soon "indicators" emerged showing that even geothermal systems not obviously associated with active volcanism might contain a considerable proportion of magmatic constituents.

In the meantime another bunch of people, called geologists, approaching hydrothermal systems from the opposite side, that of mineral or even ore deposition, found increasingly convincing evidence of a magmatic connection. By the way, according to Noel White (pers. commun.), a mineral deposit becomes an ore deposit only if people are prepared to buy shares in it. In order not to compromise themselves too much, the commitment of the geological fraternity to the magmatic cause usually consisted of more or less artistically executed magic arrows marked "magmatic fluid" or even less specific "magmatic input," pointing up from some nether regions where anything could happen. Figures 1 and 2 represent composite pictures of the two major types of these allegedly magmatic hydrothermal systems, termed for the time being, by geologists: "low sulfidation" and "high sulfidation" (Bonham, 1986; Hedenquist, 1987; White and Hedenquist, 1990). Chemists may have come up with a classification of these systems into "near-neutral, reduced" and "highly acid, oxidized" systems and associated fluids possibly into mature and immature, or "benign" and "virulent" (Reyes, 1990, 1991). I want to leave it to future generations to find the most suitable terms. Actually, I am not sure what the term "low sulfidation" refers to. Here I apply it to both epithermal and mesothermal systems, including porphyry metal deposits.

Anyway, both Figures 1 and 2 have their "mag(mat)ic" arrows in place. In this talk I will try to put some meat onto them, by delineating the possible origin of the "fluids" involved, their chemical evolution in hydrothermal systems, and the effects of various modes of magma degassing on mineral deposition. Most of the bits and pieces I am presenting here have been taken from a vast inventory of earlier studies and models of these systems, such as those of Bunsen (1847), Krauskopf (1957), White (1957), Lowell and Guilbert (1970), Holland (1972), Sillitoe (1973), Whitney (1975), Cathles (1977), Henley and McNabb (1978), Bethke and Rye (1979), Burnham (1979), Skinner (1979), Henley and Ellis (1983), Sillitoe and Bonham (1984), Eugster (1985), McKibben and Elders (1985), Hayba et al. (1986), Stoffregen (1987), Hedenquist (1987), White and Hedenquist (1990), Candela (1991), and Hemley and Hunt (1992), to name some. All I am trying to do is stick them together with some glue extracted from chemical and isotopic analyses of quite a pile of geothermal and volcanic water and gas samples. Having worked now in New Zealand for more than 20 years, right astride a convergent plate boundary and at the southwestern end of the horseshoe of fire around the Pacific, my experience is somewhat tainted by this close association with hydrothermal systems typical of this kind of tectonic environment.

Nature and Origin of Magmatic Constituents

By far the most convincing evidence of a largely nonmagmatic origin of geothermal waters was provided by the finding of Craig (1963) that all the waters available to him then had the same deuterium (D) content as local ground water. If one or even several "magmatic" waters existed, it would be too much of a coincidence if all their D contents were to agree with those of local ground waters. During an earlier investigation into the isotopic composition of steam discharged from high-temperature fumaroles on White Island (Stewart and Hulston, 1975), D and 18O contents defined a trend suggesting formation through equilibrium evaporation of a seawater-derived brine. I kept on collecting fumarolic condensates and found a similar trend, but one which pointed to the existence of a highly 18O-enriched end-member component with a D content in the vi-
MAGMA DEGASSING AND MINERAL DEPOSITION IN HYDROTHERMAL SYSTEMS ALONG CONVERGENT PLATE BOUNDARIES

The deuterium content of water from various volcanic systems is shown in Figure 3.

![Diagram](image)

**Figure 3.** Deuterium versus $\delta^{18}O$ contents for geothermal waters and volcanic condensates, together with associated local ground waters. Data from Giggenbach (in press).
1990). The first process involves quite high temperatures and leads to the formation of amphiboles, zeolites, chlorite, and serpentinite with typical D fractionations in the vicinity of 60 per mil, that is, the minerals are isotopically depleted by this value with respect to seawater (Cole et al., 1987). Incorporation into sedimentary clays is accompanied by a smaller D fractionation of about 30 per mil (Liu and Epstein, 1984), while pore water may be expected to retain its isotopic composition. An “andesitic water” with a δD value of around −20 per mil could simply represent mixtures of these waters in albeit quite narrowly defined proportions. A more likely possibility is formation of the andesitic water preferentially from the sedimentary clay fraction (Giggenbach, in press). The marine clays are carried on top of the subducting slab and, depending on the angle of subduction, varying proportions may be scraped off to form the accretionary wedges. A considerable fraction of subducted sediments, however, may reach the mantle environment. There, they are early on exposed to conductive heating from the mantle wedge leading to preferential mobilization of sedimentary volatiles and their incorporation into rising andesitic magmas. The more deeply buried water associated with the hydrated basalt may reach deeper levels to replenish the reservoir of mantle water with its lower D content.

Exsolution of water from a magma is accompanied by minor but significant isotopic fractionation (Taylor, 1986). Assuming a reasonable value of about 20 per mil, the evolution of D contents during exsolution corresponds to the trends depicted in Figure 5. Two degassing processes are distinguished: closed-system degassing generally governing underground vapor-liquid fractionation processes (Taylor, 1986), and open-system degassing typical of surface degassing during eruptions. In both cases, the “early” vapor—that produced at small vapor/melt volume ratios ($R_v$)—is enriched in D by the value of the fractionation factor. From $R_v$ values of 0.01 onward,
significant amounts of water are transferred to the vapor phase and both the D content of the vapor and of the residual melt decrease. These decreases are much more rapid in the case of open-system degassing, and D contents for both vapor and residual melt can reach very low values. The D contents of waters in usually subaerially erupted andesitic lavas, therefore, are unlikely to be representative of those of the original parent magmas. In the case of closed-system degassing underground, the D content of the vapor approaches that of the dissolved water at R$_D$ values > 1.0, that is, when the volumes of coexisting vapor and melt become about equal. The range of δD values generated by this process agrees with that delineated by the isotopic compositions of volcanic and geothermal waters as shown in Figure 3.

Water is not the only volatile present in subducted sediments. Another major source of volatiles is sedimentary carbon (Peacock, 1990). Its remobilization can be expected to give rise to increased CO$_2$ contents of andesitic vapors. A comparison of relative H$_2$O and CO$_2$ contents of volatiles uncontaminated and contaminated by subducted sediments is carried out by use of Figure 6. Uncontaminated vapors are assumed to be represented by volatiles associated with basaltic magmatism, as extracted from Mid-Atlantic Ridge “popping rocks” (PR; Javoy and Pineau, 1991) and discharged from high-temperature fumaroles within the Sierra Negra caldera (SN) on the Galapagos hot spot (W. F. Giggenbach and R. J. Poreda, in prep.). “Contaminated” vapors are represented by gases collected from high-temperature fumaroles (>300°C) on the andesitic volcanoes Satsuma Iwojima (SI) and Mount Usu (MU), Japan; White Island (WI) and Ngauruhoe (NG), New Zealand; Pandayan (PP), Indonesia; and Vulcano Island (VU), Italy (Giggenbach et al., 1990).

All the samples shown have $^3$He/$^4$He ratios more than five times those in air, indicating that the He is essentially of mantle origin. Helium may therefore be used as a reference to measure other than mantle contributions to a magmatic gas. In spite of their derivation from two quite different tectonic environments, a mid-ocean ridge and a hot spot, the compositions of the two “basaltic” gases are quite similar, with an average H$_2$O/He ratio of 26,000 and a CO$_2$/He ratio of 30,000. The averages for the six “andesitic” gases are about a hundred times higher for H$_2$O/He, at 2,720,000, and some five times higher for CO$_2$/He, at 150,000. All these samples are from high-temperature (>400°C) fumaroles; dilution by cooler crustal or ground waters, therefore, can only be minor. The internal consistency of the patterns suggests that “andesitic vapors” have intrinsically higher H$_2$O and CO$_2$ contents. The most likely sources of this excess H$_2$O and CO$_2$ are again subducted marine sediments (Giggenbach, 1992).

Another ubiquitous constituent of volcanic and geothermal vapor discharges is N$_2$. Already in 1978, Matsuo et al. ascribed highly increased N$_2$/Ar ratios (>500) with respect to air (53) to the addition of N$_2$ from subducted sediments. By plotting relative N$_2$, He, and Ar contents for both andesitic and basaltic vapors (Fig. 7), the two groups can be shown to occupy distinct positions (Giggenbach, 1992). Again N$_2$/He ratios for the andesitic vapors are considerably higher (>1,500) than those of the basaltic vapors (<250). Accepting that all the excess amounts of H$_2$O, CO$_2$, and N$_2$ are derived from subducted sediments, only about 1 percent of the water and <20 percent of the CO$_2$ and N$_2$ in vapors associated with andesitic magmatism are of mantle origin. Because of
the involvement of large proportions of subducted marine constituents, a considerable part of the S and Cl in vapor discharges from andesitic volcanoes is likely to be of a similar origin.

Once entrained into the rising andesitic magma, the volatiles will react with one another and the rock in response to decreasing temperatures and pressures to produce the variety of gases encountered at the surface in volcanic and geothermal areas.

Chemical Evolution of Volatiles

The close association of geothermal systems with volcanic systems has long been recognized (Bunsen, 1847). In 1957, White provided a classification of the major types of volcanogenic waters and suggested processes that may account for their compositional differences. The two major chemical variables controlling the composition of aqueous fluids and their interaction with rock are redox potential and acidity. I use the term "fluid" only reluctantly, as its indiscriminate use is one of the indicators that someone doesn’t know what he/she is talking about, or can’t make up his/her mind whether it’s a vapor or liquid. If at all possible one should use the more specific terms “liquid” or “vapor”; after all, they have quite different properties and behave quite differently. You may also notice that I use the somewhat vague expressions “redox potential” and “acidity” when I could have used, e.g., \( f_{\text{O}_2} \) and pH, terms having a much more distinct, if not distinguished ring about them.

When I accepted the invitation to give this lecture, I asked SEG what they wanted me to talk about, and they replied: anything you like, it is your chance to get things off your chest, things you would never say in a formal paper (also, of course, providing an excellent chance to make a fool of myself). If they only had known. I am conducting a number of minor pet crusades. One of them is “fighting” the use of \( f_{\text{O}_2} \) and variables of a similar ilk, such as \( f_{\text{H}_2} \), Eq, in connection with hydrothermal systems. You may ask, why bother, after all they are only convenient ordering parameters, “master variables,” very useful in the depiction of the relative stability of mineral and other phases.

What does it matter that there is only about one-tenth of an \( \text{O}_2 \) molecule in a km\(^3\) of water in equilibrium with crustal rocks at 250°C? What does it matter, we might as well use praseodymium (II/III) ratios, thermodynamically they are all equivalent. The thing is, of course, that we are doing geochemistry and not thermodynamics and thermodynamics is only a tool to be adapted to our needs and not the other way round. We want to find out who does what to whom and when, and \( \text{O}_2 \) does nothing, to nobody, never, in your average hydrothermal system. But people argue we can measure it, we have, e.g., electrodes which respond to it. Whom are they trying to kid? These electrodes measure anything but \( f_{\text{O}_2} \). I want to see the electrode capable of sensing one-tenth of an \( \text{O}_2 \) molecule in 1 km\(^3\) of solution. What it sees is perhaps \( f_{\text{H}_2} \), the Fe(II)/Fe(III) or Mn(II)/Mn(III) activity ratio, but not \( f_{\text{O}_2} \). So why use something of no relevance? Are our brains so corroded by thermodynamics or are we so blinded by the apparent elegance, or rather arrogance of these concepts? As with any other set of principles, belief systems, or religions, thermodynamics, if pushed too far, can lose its contact with reality and become meaningless. Thermodynamics simply doesn’t worry about atoms and kinetics, real life is all atoms and kinetics.

And it does matter. Only yesterday, I went to a talk where it was argued that the main advantage of using \( f_{\text{O}_2} \), even in low-temperature diagenetic systems, is its strong temperature dependence. I fully agree, \( f_{\text{O}_2} \) would make a perfect geothermometer, if it could be measured. Any lower temperature (<$300^\circ$C) \( f_{\text{O}_2} \), however, is always obtained only indirectly, by use of a conversion reaction such as

\[
\text{H}_2 + 0.5\text{O}_2 = \text{H}_2\text{O}. \tag{1}
\]

By expressing redox potentials in terms of \( f_{\text{O}_2} \), we simply multiply in the steep temperature dependence of a conversion reaction and nothing is gained. It is the same as looking into your wallet with a magnifying glass and thinking you have more money.

Use of these master variables is often only a cop-out and another good indicator that people don’t know what is really going on, in this case which variables actually control redox potential or acidity. It is so easy to say: when the \( f_{\text{O}_2} \) or pH goes up or down, such or such happens, but it doesn’t tell one how, and what, and when. To get these answers we have to write our reactions in terms of actual reaction participants, which sometimes may not be easy. But by forgetting about these cop-out variables, \( f_{\text{O}_2} \), \( f_{\text{H}_2} \), Eq, and even pH, we are forced to look for the real reaction participants. The use of nonexistent, practically irrelevant reaction participants is probably justified if we see chemical equations only as energy balances and neglect the dualistic character of the law of mass action, according to which a chemical equation is always also a mass balance. The reaction

\[
2\text{Fe}_3\text{O}_4 + 0.5\text{O}_2 = 3\text{Fe}_2\text{O}_3 \tag{2}
\]

may proceed on contact with air, but not deep within a hydrothermal system;

\[
2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} = 3\text{Fe}_2\text{O}_3 + \text{H}_2 \tag{3}
\]

does.

After all this noise, it is probably up to me now to show which variables to use and how to find them. Nature only reveals her secrets if we ask the right
questions and listen, and listening in geochemistry means sampling, analyzing, plotting. Before going any further, I may be allowed to offer some more recipes for successful listening. “Plotting” should be based on data as measured, corrected for obvious errors, but otherwise unencumbered by frequently unjustified assumptions. Use of conversion reactions to convert a measured variable to intellectually ever so appealing “master variables” is always based on the implied assumption that all reaction participants were in equilibrium at some stage and that they are still present in proportions representative of this hypothetical equilibrium, which is not at all guaranteed. Measured variables and theory should be kept strictly separate. This is most readily done by choosing graphs with coordinates representing only measured, or at least measurable, values, such as concentrations and temperatures, and packing all theory into the space outlined by the coordinates. Also, one should try to preserve the identity of each measured variable as much as possible by choosing combinations involving at most two variables, such as a ratio. Ratios also have the major advantage of being dimensionless and therefore being independent of absolute concentrations. In the case of geologic, frequently quite dynamic, systems, combination of more than two variables into complex concentration or activity quotients greatly increases the uncertainty in the relevance of the values obtained. A typical example is the Fischer-Tropsch reaction according to:

$$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}. \quad (4)$$

$\text{CO}_2$ may be controlled by formation of calcite at deeper levels, $\text{H}_2$ by interaction with $\text{Fe}^{2+}/\text{Fe}^{3+}$ of the rock up to quite shallow levels, whereas $\text{CH}_4$ may result from the decomposition of sediments in an entirely different environment. Forming the complex concentration quotient $x_{\text{CH}_4} x_{\text{H}_2\text{O}}/x_{\text{CO}_2} x_{\text{H}_2}$ presupposes that all four components are present in our sample in amounts representative of attainment of equilibrium at some stage. As measured, they probably never are and never were in equilibrium. There I have to confess to sins of my younger, less enlightened years (Giggenbach, 1980). So, what then is the use of a “master variable”? With these minor details settled, we can try to find out what’s really going on.

Like those TV cooks, I have all the ingredients already in little bowls, in this case diagrams, and we can dispense with the preliminaries, such as sampling, analyzing, and interpreting. To do the latter, it is usually a good policy to look at the behavior of the major species first. After all, they are most likely to be part of major buffer systems or to dominate the chemical environment. In the case of volcanic gases, they are, after water, $\text{CO}_2$, sulfur in its various oxidation states, and HCl. In Figure 8, I plotted them in terms of relative $\text{H}_2\text{O}$-HCl versus relative $\text{SO}_2$-$\text{H}_2\text{S}$ values for volcanic vapor discharges from White Island, New Zealand (Giggenbach, 1987) and other volcanoes mentioned earlier (Giggenbach et al., 1990). There are of course dozens of other ways to plot these chemical compositions. The major advantage of plots involving concentration or mole fractions, such as Figure 8, over ratio plots is the possibility of plotting pure components, as they treat all four variables equally and none has to play denominator. Also, two-component mixing is always represented by straight lines.

Geothermal vapors are represented by only one point in the upper right corner of the diagram, as they usually don’t contain $\text{SO}_2$ and HCl. High-temperature (>300°C) volcanic vapors occupy positions in the lower left sector reflecting their highly oxidized nature and high HCl contents. Lower temperature discharges appear to fall into two groups: one reflecting removal of HCl but remaining oxidized, the other with most of the S reduced to $\text{H}_2\text{S}$, at a minor loss of HCl. It is obvious that the two major processes responsible for the conversion of volcanic-magmatic to geothermal “fluids,” removal of HCl by conversion to a metal chloride, and reduction of $\text{SO}_2$ to $\text{H}_2\text{S}$, may operate quite independently, but in the end give the same results: the formation of near-neutral, reduced “geothermal” fluids.

HCl is a strong acid and the most likely process leading to its removal is neutralization through interaction with oxidic components of the rock phase. As pointed out above, geochemical processes are best evaluated in terms of reactions involving actual reac-
tion participants and on the basis of dimensionless variables, such as concentration ratios. The variable to be combined with $m_{KCl}$ to form a ratio should also be a major component of the entire system. In the present case, the most suitable is $m_{KCl}$. A graphic representation of possible reactions of HCl with minerals of the rock phase to form KCl, as a function of temperature, is given by Figure 9. It is based on data reported by Sverjensky et al. (1991).

In an earlier investigation (Giggenbach, 1984), the two limiting processes governing the interaction of magmatic volatiles with crustal rock were suggested to correspond to initial isochemochemical dissolution of the rock by the highly aggressive waters formed through absorption of the volatiles into deeply circulating ground water and to eventual equilibration of these waters with a mineral assemblage resulting from isochemochemical recrystallization of the original rock. In hydrothermal systems, the overall process consists essentially of the conversion of framework silicates, such as feldspars, to layer silicates, such as micas and clays.

In Figure 9, trajectories are shown representing these two end-member processes. Assuming the gases, released at magmatic temperatures, to be absorbed directly into cooler ground water, without any further interaction with rock, magmatic HCl/KCl ratios are maintained and the cooling trajectory corresponds to the horizontal path (a). On the other hand, if the evolved vapors rise more slowly in sufficient contact and equilibration with the rock, increasing amounts of HCl are converted to alkali chlorides through interaction with feldspars to form layer silicates according to:

\[
1.5 \text{feldspar} + \text{HCl} \rightleftharpoons 0.5 \text{mica} + 3 \text{silica} + \text{KCl}
\]

and the system may follow another path such as (b). For solutions remaining in full equilibrium with the rock, the ratio HCl/KCl drops from a value of about 0.1 at 600°C, to 0.01 at 500°C, and to 0.001 at 400°C. At 100°C, >99.9 percent of the initial HCl is converted to a metal chloride. The resulting waters are neutral Cl waters typical of "mature" geothermal systems, path (d).

In the case of the rapidly cooled waters, high initial HCl/KCl ratios are preserved and the waters become highly reactive with regard to alteration of primary rock. Corresponding alteration products are highly cation-depleted minerals such as pyrophyllite and kaolinite. For acidities high enough, the process may lead to complete cation leaching with only silica remaining. At sufficiently high sulfate concentrations, alunite will form from even highly acid solutions. In nature, actual interaction with rock may follow an intermediate path, such as (b) crossing the stability fields of micas, as shown.

Figure 9 also provides a good illustration for the need to select the most relevant variables. Using HCl and KCl, species actually consumed and produced, an immediate quantitative assessment of the process can be made. Another popular variable in the construction of thermodynamic stability diagrams is the activity ratio $a_{\text{HCl}}/a_{\text{KCl}}$. Corresponding stability boundaries, according to Sverjensky et al. (1991) are also shown in Figure 9 by dashed lines. The change in $a_{\text{HCl}}/a_{\text{KCl}}$ is much smaller for full equilibrium interaction along the feldspar-mica boundary than that in $m_{\text{HCl}}/m_{\text{KCl}}$. It could wrongly be interpreted to mean

\[
\text{FIG. 9. Stability of aluminum silicates as a function of temperature and } L_{\text{KCl}} = \log \left( \frac{m_{\text{HCl}}}{m_{\text{KCl}}} \right) \text{ according to Sverjensky et al. (1991). Dash-dotted lines represent solution paths as discussed in text.}
\]
that interaction of acid volcanic waters with rock is accompanied by only small amounts of alteration because the activity ratio of the “reactants” remains almost constant. At temperatures > 300°C, acids are increasingly associated and H+ becomes a very “unimportant” species, unsuitable to be used as a quantitatively relevant, “actual” reaction participant.

Purely on the basis of Figure 9, interaction of originally magmatic volatiles with rock at lower temperatures is able to generate a wide range of geochronological environments depending on temperature and duration of interaction with rock contacted.

According to Figure 8, the other major process accompanying conversion of magmatic volatiles to geochemical fluids, is reduction of SO₂, and other oxidized S species, to H₂S. Again, by defining a variable, involving actual and measurable reaction participants, H₂ and H₂O, the limiting processes governing redox reactions in volcanic systems were found to be equilibration with the major redox pair of the vapor phase H₂S–SO₂, and with Fe(II)–Fe(III), the major redox system of the rock phase (Giggenbach, 1987). In lower temperature hydrothermal systems, SO₂ can be expected to disproportionate into H₂S and a sulfate species and redox buffering is likely to be due to these species, as shown in Figure 10. It was drawn by use of thermodynamic data for minerals provided by Bowers et al. (1984) and for solute species by Murray and Cubicciotti (1983).

Depending on the degree of neutralization of the solutions, the H₂S–sulfate buffer lines move with decreasing acidity to higher values of $R_{H} = \log \left( \frac{f_{H_2S}}{f_{SO_2}} \right) \simeq \log \left( \chi_{H_2S} \chi_{SO_2} \right)$, where f and $\chi$ are the fugacities or vapor phase concentrations of the species i. Optimum efficiency of a buffer is achieved when both components are present in comparable amounts, not activities. Nevertheless, the lines shown in Figure 10 are based on more “easily” estimated activity ratios. Accepting these lines to reflect buffer trends, a number of likely paths, taken by fluid mixtures during their rise from a magmatic environment to the surface, can be drawn (Giggenbach, 1991).

Again, assuming the vapor released from the magma to be cooled rapidly, without significant interaction with the rock, the redox potential is determined by internal equilibration among the fluid phase components and the system moves down the “gas buffer” line. At lower temperatures, H₂SO₄ will disproportionate into H₂S and a sulfate species. The positions of the H₂S–sulfate isoactivity lines depend on the degree of neutralization of the solutions. Their general directions, however, remain similar and the path of a rising fluid will change from the trend marked by the gas buffer to one parallel to an H₂S sulfur isoactivity contour, paths (b) or (c).

Figure 10 also contains stability boundaries for a number of minerals. Alunite is likely to form only at very low values of $R_{H}$ and therefore only from solutions cooled rapidly, such as those generated by absorption of volcanic vapors into shallow ground waters or crater lakes, path (a). The coexistence of pyrite and alunite in the Summitville “high sulfidation” ore deposit at temperatures of 250°C (Stoffregen, 1987) fixes its position in Figure 10. In the case of more slowly rising waters, acidities may be reduced sufficiently to allow anhydrite to form (path b). Even more slowly rising waters soon leave an early zone of formation of a sulfate mineral and most of the S is deposited as pyrite (path c). At $R_{H} > -4$, the buffer capacity of the H₂S–SO₄ system is heavily impaired as by far most of the SO₄ is converted to H₂S, and solutions should have no problems to attain full equilibrium with the Fe(II)–Fe(III) “rock buffer.” The presence of both pyrite and pyrrhotite at 300°C places the point for the Ohaaki geothermal system right on the rock buffer line. It may have reached this position by following path (d).

Assigning comparatively well-defined positions to these systems, however, is highly misleading. Within each of these systems, microenvironments are likely
to exist spanning the entire range of \( R_{\text{H}} \) values, from highly oxidizing to full equilibrium with the rock buffer. The entire set of processes occurring may be compared to a tennis game with the two players represented by the two major buffers. A given subsystem may represent the ball moving between the two, with thermodynamics providing the rules and mass balances the lines on the ground. Any thin section of a rock sample taken from anywhere within the system then may contain a series of “snapshots” of the position of the ball in either court. A veinlet may at some stage be exposed to a good flow of fluid, thus recording “fluid-dominated” alteration processes. Once it becomes blocked, the trapped solutions may have time to react and the same subsystem converts to a “rock-dominated” alteration system. The rapid changes in equilibration conditions among minerals and solutions are well documented by drastic zoning, for instance, in the isotopic composition of sulfide minerals as detected by SHRIMP (McKibben and Eldridge, 1990). Rather than being due to global changes affecting the entire system, they may simply be due to local changes in fluid flow. In the case of the S isotopes, the drastic changes may reflect varying degrees of reduction of the initially oxidized magmatic sulfur. At low degrees of reduction, close to path (a), the small amounts of sulfide formed are very depleted in \(^{34}\text{S}\), with increasing reduction, the composition of any sulfides formed approaches that of the original magmatic sulfur. The isotopic compositions of the sulfides then may simply record oscillations between these two end-member situations. No external input, such as inflow of oxygenated ground water, or major changes in steady-state physical and chemical conditions, such as boiling, as frequently invoked, would be required.

The above discussion covers the possible origin of fluid phase constituents associated with adesitic magmatism and chemical pathways traveled by the fluid mixtures from a degassing magma body through the crust. Not much has actually been said yet about the actual mode or modes of magma degassing, the true nature of the “magmatic arrows” of Figures 1 and 2.

**Modes of Magma Degassing**

According to Figures 9 and 10 one might conclude that the evolution of magmatic to hydrothermal, or geothermal, fluids is a continuous process. In this case we should observe an entire spectrum of epithermal mineral deposits, from highest to lowest sulfidation, so to speak, and also transitional systems where, e.g., a high sulfidation deposit evolves into something resembling a porphyry copper deposit or vice versa. At a meeting organized by the Geological Survey of Japan on “High Temperature Fluids and Associated Alteration and Mineralisation” (Matsuhiwa et al., 1991), it was the general lack of such intermediate and transitional systems which alerted us to the possibility that the formation of these two types of epithermal mineral deposits must be controlled by additional factors, not just the temperature and degree of magma degassing but possibly also the mode of magma degassing itself.

The most obvious and rapid mode of degassing of andesitic magmas is that accompanying volcanic eruptions such as those recently from Mount Saint Helens, Nevada del Ruiz, and Mount Pinatubo. In these cases, the volatiles are released directly into the atmosphere and any interaction with cooler rock and ground water is very limited. During periods of less violent, fumarolic activity, high-temperature volatiles may still be released from deeper lying, but freely degassing, “boiling” magma bodies. Depending on the depth to the degassing magma body, the configuration and permeability of the gas conduits, and hydrological conditions, some of the gases may be prevented from escaping directly and may start to interact with local ground water to form a crater lake such as at Mount Ruapehu, New Zealand (Giggenbach, 1975), El Chichón, Mexico (Casadeval et al., 1984), Sirung, Indonesia (Poorter et al., 1989), and Poás, Costa Rica (Oppenheimer, 1992), or secondary volcanic waters as discharged from highly acid and mineralized ClSO\(_4\) springs within the crater (Giggenbach, 1987; Poorter et al., 1989) or the outer slopes of a volcanic structure (Giggenbach et al., 1990). The minerals forming from these waters include gypsum or anhydrite, alunite, pyrite, and a silica polymorph. At El Ruíz, a thick deposit of an amorphous As-Sb sulfide was observed along a spring channel (Giggenbach et al., 1990).

In these volcanic systems, formation of mineralized waters may consist of direct absorption of magmatic volatiles, possibly released from such subterranean “lava lakes” (Giggenbach, 1987; LeCloarec et al., 1992) into local ground water at comparatively shallow levels. Their acidity and redox potential correspond to those indicated by paths (a) in Figures 9 and 10. With increasing depth to the degassing magma body, maintenance of a freely degassing lava surface and associated open conduits becomes increasingly difficult and at some stage the degassing magma body will become sealed by the formation of a shell of solidifying rock. Over its inner parts, this shell remains plastic and therefore impermeable to volatiles (Carrigan, 1986; Goldfarb and Delaney, 1988). Under these circumstances, direct transfer of magmatic volatiles to circulating ground water is impeded and a different degassing mechanism is required.

As the encased magma body cools, volatiles are likely to accumulate on top of the still liquid interior (Candelori, 1991) to be incorporated into a volatile-saturated carapace as discussed in detail by Burnham
(1979). On further cooling the boundary of solidifying magma retreats to lower levels and the trapped volatiles become incorporated into increasingly cooler and rigid layers of volcanic rock. If the volatile contents of the cooling magma were high enough, part of the volatiles may exsolve to accumulate in vesicles.

From a given temperature downward, the mechanical strength of the still hot rock increases sufficiently to give rise to brittle fracturing allowing some of the stored fluids to escape or external fluids, ground water, to penetrate as evaluated in detail by Lister (1974). Other models of the processes governing the distribution of temperatures and fluids around cooling magma bodies have been presented by Whitney (1975), Cathles (1977), Burnham (1979), Hardee (1982), and Carrigan (1986). Fournier (1992) puts the temperature of transition from plastic to brittle behavior in silicic rocks as low as 400°C to 375°C.

According to the above evaluation, there exist two distinct thermal regimes governing the release of magmatic volatiles: that associated with freely degassing surfaces of liquid magma at temperatures > 1000°C, the other with brittle fracturing in solidifying rock at temperatures < 400°C. In the latter case, volatiles stored in vesicles or along grain boundaries may be released in two ways: at shallow levels where hydrostatic pressures are low, they may escape partly in vapor form, to be absorbed later into shallow ground water; at greater depths, “degassing” resembles more a leaching process of originally magmatic volatiles, or their reaction products with the rock, by more highly pressured, deeply circulating ground water. The assumption of release of originally magmatic volatiles by the latter process also bridges the gap between two major theories advanced to explain the origin of hydrothermal solute species: rock leaching as proposed by Ellis and Mahon (1964) and magma degassing by Krauskopf (1957), Holland (1972), Burnham (1979), and Eugster (1983). Release of the originally magmatic volatiles, partly stored in vesicles, into minor amounts of invading ground water may lead to the formation of highly saline solutions and gassy vapors and corresponding fluid inclusions, as frequently observed over the central parts of hydrothermal systems or ore deposits (Roedder, 1971; Reynolds and Beane, 1985; Reyes, 1990; Bodnar, 1992).

In addition to the marked differences in the temperature of volatile “exsolution,” the composition of the volatiles associated with the two major types of magma degassing may also be quite different. Basaltic magmas were shown to become saturated with respect to dissolved gases at a depth of around 50 km (Bottinga and Javoy, 1980). Andesitic magmas, with their probably much higher volatile contents, can be expected to start to “boil” at even greater depth. By the time the magmas are erupted at the surface, far the largest proportions of the original volatiles have left the melt phase; any volatiles subsequently extracted from accessible samples of solid material, such as volcanic glass, melt inclusions, or crystals, therefore, are likely to represent only a very minor residual fraction of the original “andesitic volatiles.” Both isotopic and chemical compositions will be heavily modified by fractionation processes accompanying such extensive vapor exsolution. Even volcanic gases collected from high-temperature fumaroles are unlikely to be fully representative of the volatile contents of the original andesitic magmas but may give an indication of the composition of vapors in equilibrium with andesitic magmas at comparatively shallow levels, levels similar to those of emplacement of the magma bodies driving hydrothermal systems. By “calculating back,” the compositions of potential melts coexisting with fumarolic gases may be evaluated as shown in Figure 11.

The composition of vapors released from andesitic volcanoes is represented by six data points taken from the same compilation as those shown in Figure 8. Their average composition corresponds to mole ratios of CO₂/S/HCl = 10:3:1. They are all produced from probably very shallow bodies of magma, at low pressures, and the vapor/melt volume ratios accompanying vapor exsolution can be assumed to be very high, >10. In this case most of the even more soluble components, S and HCl, should have partitioned into the vapor phase and the composition of fumarolic gases becomes very similar to that of the volatiles originally dissolved in the deep magma. Accepting that the composition of volcanic gases, as sampled,
may resemble closely that of the volatiles originally dissolved, the compositions of volatiles in the resid-
ual magma, coexisting with these vapors, were calculated, as a function of $R_v$, the vapor/melt volume ra-
tio, by techniques described in detail by W. F. Gig-
genbach and R. J. Poreda (in prep.). Even for low
values of $R_v$ of $<0.1$ (vesicularity $< 11\%$), relative
$CO_2$ contents of the residual magma drop rapidly at
constant S/Cl ratios. When values of $R_v$ exceed 1 (vesi-
cularity $>50\%$), increasing proportions of S parti-
tion into the vapor phase and the residual magma be-
comes very $CO_2$ and S poor, and relatively Cl rich.
The compositions of vapors released from an anodesi-
tic magma are given by the curve marked “vapor.”
Recently a number of investigations involving $H_2O$
and Cl have been carried out; they allow a much
more comprehensive and detailed evaluation of va-
por-melt distribution processes accompanying magma
degassing (Shinohara et al., 1989; Metrich and Ruth-
erford, 1992; Webster, 1992).

The point marked “degassed melt” represents the
volatil mixture remaining dissolved in the residual
rock after extensive closed-system degassing. The
major parts of the volatiles released from a magma at
depth reside in the vesicles; their composition is
likely to resemble closely that released from fuma-
roles. This distinction is important when it comes to
comparing the isotopic and chemical composition of
“free volatiles” and those extracted from andesitic
solids, such as glasses or melt inclusions. They can in
no way be compared directly. Following incursion of
depth circulating ground waters, the volatiles dis-
solved in the rock matrix and stored in vesicles are
released to form highly saline solutions and gas-rich
vapors to be trapped in “hypersaline” and $CO_2$-rich
fluid inclusions (Bodnar, 1992), partly reflecting the
composition of the originally magmatic vapors.

Summing up, formation of an impermeable shell
around cooling magma bodies leaves only two “win-
dows” for the evolution of magmatic volatiles. The
high-temperature window is only able to remain
open for magma bodies emplaced at shallow levels
and gases are released directly to the atmosphere.or
into shallow ground water. The other window opens
once the temperature has become low enough for
brittle fractures to form, allowing some of the
trapped volatiles to escape or to be “leached” by in-
vading ground water. The existence of these two dis-

tinct modes of degassing may give rise to two distinct
modes of mineral deposition.

Modes of Mineral Deposition

One of the most obvious differences in the two ma-

jor modes of magma degassing is the temperature of
volatile release: $>1,000^\circ C$ in the case of free release
from a “boiling” magma surface, $<400^\circ C$ in the case
of subsolidus degassing. Based on isotopic and fluid
inclusion evidence, however, the temperatures of
mineral deposition are with $250^\circ C$ to $350^\circ C$, very simi-
lar for both high and low sulfidation, epithermal ore
systems (Stoffregen, 1987; White and Hedenquist,
1990). The marked differences in the mineralogies of
high and low sulfidation ore deposits therefore are
likely to be due to differences in the modes rather
than the temperatures of mineral deposition. Again,
the chemical processes are probably best discussed
separately in terms of those controlling acidity and
redox potential.

The likely path of solutions resulting from direct
degassing of a magma at high temperatures and ab-
sorption into cooler ground water is marked (a) in
Figure 9. At magmatic temperatures, the fluid is in
equilibrium with its mineralogical environment and
any alteration of primary rock by circulating fluids is
likely to be restricted to isochemical recrystallization
or to minor K metasomatism of the rocks contacted
(Giggenbach, 1984). Depending on the extent of
these early reaction zones, the system may follow an-
other path (b) with initially high magmatic $m_{H_2O}/m_{K_2O}$
ratios lowered to varying degrees. Generally, the ris-
ing solutions become, with decreasing temperature,
increasingly reactive with respect to rock alteration
or more specifically H metasomatism. Initially the al-
teration products will be those typical of phyllic alter-
nation, such as micas. At lower temperatures, the min-
erals forming in the now highly acidic systems are
highly cation-depleted phases such as pyrophyllite,
kaolinite, or at the usually very high $SO_4$ contents,
alunite. At sufficiently low temperatures, the solu-
tions may become aggressive enough to give rise to
complete rock destruction and removal of all cationic
components including Al and Fe, leaving only a resi-
due of “vuggy” silica typical of high sulfidation ore
deposits (Stoffregen, 1987; Izawa, 1991). The para-
genetic relationships implied by paths (a) and (b) in
Figure 9, correspond exactly to those observed at
most of these systems with decreasing depth (White
and Hedenquist, 1990; Izawa, 1991). Examples of
the aggressive solutions formed in these volcanic sys-
tems are the highly acid and mineralized waters dis-
charged from springs on White Island (Giggenbach
and Glasby, 1977) and Nevada del Ruiz (Giggenbach
et al., 1990) or present in volcanic crater lakes (Gig-
genbach, 1975; Oppenheimer, 1992; Casadeval et al.,
1984).

For the volatiles trapped in the solidifying shell
surrounding a cooling magma body, prolonged and
persistent contact with rock at decreasing tempera-
ture should favor maintenance of, or at least close
approach to, fluid-rock equilibrium and the system
may follow path (d), including the stretch marked
“fluids trapped in solidifying magma.” They are only
released once the system reaches the point marked
“brittle fracturing.” By this time >95 percent of any
magentic HCl may have been converted to an alkali chloride. Any free vapor released, therefore, will be much less aggressive with respect to rock dissolution than those released under magmatic conditions. Any liquid phase remaining in the rock will be highly saline and very similar to the hypersaline fluid inclusions as frequently observed in drill cores from wells into volcanic hydrothermal systems (Reyes, 1990; Reyes and Giggenbach, 1992) or in samples from hydrothermal ore deposits (Roedder, 1971; Reynolds and Beane, 1985).

As stated above, the relative proportions of the fluids released in the form of vapor or leached by circulating ground water will depend on the depth to the degassing magma body. At shallow levels, or high within a volcanic structure, hydrostatic pressures are comparatively low and volatiles are likely to be released as vapors followed by absorption into cool ground water. This process was assumed to lead to the formation of the comparatively acid, high sulfate waters discharged over the outer slopes of the El Ruiz (W. F. Giggenbach and R. J. Corrales, in prep.) and Miravalles volcanic structures (Giggenbach, 1992). The path taken by these fluids, in Figure 9, is likely to approach that of a horizontal line extending away from the point marked “brittle fracturing” to lower temperatures, path (c).

At greater depths, increasing hydrostatic pressures will aid penetration of ground water, facilitating hydrothermal alteration and “leaching” of the trapped, originally magmatic volatiles. The resulting solutions have a good chance to remain in equilibrium with the rock matrix to end up as neutral chloride waters typical of “mature” geothermal systems.

The above evaluation is based on the behavior of only one of the acid constituents of an originally magmatic vapor phase, HCl. Another important component is CO₂. The relative efficiency of these two, with respect to rock alteration, may be evaluated as a function of temperature and in terms of the amounts of feldspar converted to layer silicates. The interaction of HCl with feldspar may be represented by the reaction:

\[ \text{feldspar} + 2\text{HCl} = \text{mica} + 2\text{KCl} \]  \hspace{1cm} (6)

and that of CO₂ by

alkali feldspar + Ca feldspar + CO₂

\[ = \text{mica} + \text{calcite}. \]  \hspace{1cm} (7)

The amounts, in g, of mica formed, for a drop in temperature of 10°C, as a function of initial contents of HCl and CO₂, in g/kg of solution, and according to the above two reactions, are shown in Figure 12. At temperatures above 600°C, the solutions are inert with respect to rock alteration by either HCl or CO₂ and no mica is formed. The onset of attack by HCl is quite sudden and by far most of the HCl reacts according to reaction (6) at temperatures above 400°C. The temperature range of 400° to 600°C, of course, is within that where volatiles remain trapped within the cooling magma, facilitating neutralization of most of the acidity due to HCl before the trapped fluids are able to escape. CO₂ becomes reactive with re-

![Figure 12](image-url)

**FIG. 12.** Equilibrium amounts of K mica formed (in g) through alteration of feldspars, as a function of initial HCl and CO₂ contents of hydrothermal solutions for a drop in temperature by 10°C.
WERNER F. GIGGENBACH

14

Fig. 13. The solubility of gold, in μg/kg, as HAu(SH)_2 as a function of temperature and R_H. Dash-dotted lines represent solution paths as defined in Figure 10. Sulfate minerals are represented by either anhydrite or alunite.

spect to rock alteration only at temperatures < 330°C. Again the onset of feldspar alteration is quite sharp and peters out at temperatures below 150°C.

In addition to the two alteration regimes imposed by the mechanical strength of a cooling magma, we have two distinct regimes defined by the nature of the major acidity-controlling species: HCl at high temperatures 400° to 600°C or in solutions affected by direct absorption of magmatic vapors; CO₂ in lower temperature (<350°C) hydrothermal systems. The acidity caused by CO₂ is insufficient to give rise to the intense alteration observed in high sulfidation ore deposits. These high acidities can only be generated from magmatic fluids released at high temperatures in a way preventing strong acids from becoming neutralized at intermediate levels and temperatures. Conditions allowing strong acids to survive neutralization by interaction with rock are restricted to systems with very steep temperature gradients and therefore to comparatively shallow levels within or beneath a volcanic structure. Preliminary assessments for White Island show that the amounts of mineral components involved in these processes are sufficient to generate sizable ore deposits (Giggenbach and Glasby, 1977; Hedenquist et al., 1992).

The actual modes of mineral deposition are illustrated in Figure 13 for gold in terms of the other major variable controlling fluid-rock interaction, the redox potential. Again, the dashed lines represent likely paths of solutions rising from degassing magma bodies. In neutral to alkaline waters, Au is likely to be transported as the Au(SH)₂⁺ species (Seward, 1973); in the generally more acid solutions discussed here, the most likely species is H₂Au(SH)₂⁻ (Hayashi and Ohmoto, 1991). Instead of H₂S.SO₄ contours, Figure 13 shows contours representing dissolved Au in the form of H₂Au(SH)₂⁻, the thi-o-gold complex predominating at pH values of <5. The Au solubility contours were calculated by use of the reactions:

2Au + 2 pyrite + 3 water
= 2HAu(SH)₂⁻ + hematite, (8)

2Au + 2 alunite + 15H₂
= 2HAu(SH)₂⁻ + 2 mica + 19 water, (9)

and

2Au + 4 anhydrite + 4 kaolinite + 15H₂
= 2HAu(SH)₂⁻ + 4CaAl₂ silicate + 7 water, (10)

where hematite represents the thermodynamic proxy of Fe(II) of the rock phase. Calcium in an Al silicate is represented by CaAl₂ silicate, laumontite at low, wairakite at intermediate, and anorthite at high temperatures.

Reaction (8) is independent of the redox potential, therefore contours in Figure 13, over the pyrite stability field, are vertical and only a function of temperature. In contrast, contours based on the two reactions involving sulfate minerals, are highly dependent on R_H and virtually independent of temperature. The behavior of Au with respect to transportation and deposition can therefore be expected to be quite different in these two environments. In an environment dominated by the formation or presence of sulfate minerals, simple cooling would actually increase the solubility of Au and any Au acquired at deeper levels would remain in solution. On the other hand, in a more reduced environment, dominated by the formation of pyrite, a drop in temperature by 30°C would be accompanied by the deposition of 90 percent of the Au from any saturated solution. In nature, mineral-depositing processes rarely involve only one variable and the overall process is probably more realistically modeled in terms of the various fluid paths as derived in Figure 10.

Following path (a), the one most closely reflecting redox control by the “fluid buffer,” concordant changes in both temperature and R_H would lead to
rapid deposition of dissolved Au. For solutions following more reduced paths, such as (b) and (c), the rate of deposition of Au depends on the nature of the predominant S mineral, pyrite or anhydrite. If the latter predominates and if solution mineral equilibrium is maintained, initially saturated solutions can be expected to traverse considerable ranges of temperature where they become undersaturated again. On crossing into the pyrite stability field, however, all these solutions will lose most of their Au on further cooling, conductively or by dilution with cooler ground water. Diagrams such as Figure 13 can be constructed for any other mineral-depositing system. As I have already overdrawn my allocated time considerably, I better start summing up.

Summary and Conclusions

One of the major purposes of my talk was to throw some light, or to put some meat, onto the possible nature of the “magic arrows” generally employed to signify injection of magmatic fluids into hydrothermal systems. In the case of such systems associated with volcanic activity along convergent plate boundaries, isotopic and chemical evidence suggest that the major fluid components H₂O, CO₂, and probably Cl, may largely be derived from subducted marine sediments and seawater. Depending on the level reached by the rising, generally andesitic magmas, volatiles are degassed in two distinct modes: at magmatic temperatures from an effectively freely boiling magma either at the surface, during eruptions, or from subterranean “lava lakes”; and from the solidified shell surrounding a more deeply buried magma body in response to thermal fracturing.

The active systems likely to give rise to the formation of the mineral deposits represented by Figures 1 and 2 are shown again schematically in Figures 14 and 15. In the case of “high sulfidation” systems, part or all of the vapors degassing from a subterranean lava surface may be absorbed at shallow levels into cool ground waters leading to the formation of initially only little reactive solutions capable of phyllic to argillic alteration of primary, usually igneous rock. With decreasing temperature, the solutions become increasingly acid and oxidizing, thus promoting wholesale rock destruction and the deposition of secondary minerals such as alunite, anhydrite, pyrite, and silica. At sufficiently low temperatures, <250°C, acidities may become high enough to cause complete rock destruction with only “vuggy” silica remaining. Part of the ore-forming constituents are likely to be derived from the dissolved rock; a considerable proportion may be introduced directly with the magmatic vapor. Gold is deposited from the resulting so-
lutions, once saturated, largely in response to decreasing temperature at a rate of about 90 percent for every 30°C.

“Dry” degassing of a solidifying magma at shallow levels leads to the release of less aggressive but still acid and oxidizing vapors which, on contact with ground water, may give rise to the formation of acid Cl-SO₄ waters, typical of active volcanic systems, intensive rock alteration, and the deposition of elemental sulfur. Part of the “dryly” degassed vapors may accumulate within the volcanic structure (Giggenbach et al., 1990), to be released during eruptions, thus contributing to the large excess of volatiles frequently observed (Williams et al., 1990). Because of the limited spatial extent of these systems and the absence of metal-rich, high-temperature magmatic vapors, their potential for forming mineral deposits, except of elemental S, is probably only minor. The comparative rarity of typical volcanic hydrothermal discharges (Reyes and Giggenbach, 1992) also suggests that both their spatial and temporal extents are very limited. Nevertheless, the inclusion of even minor amounts of these acid Cl-SO₄ waters into geochemical wells drilled too close to volcanic systems may generate major problems.

Both the time and amount of source material available for the formation of significant mineral deposits can be expected to increase as zones of water-rock interaction progress to deeper and deeper levels. Figure 14 also presents the distribution of fluids in a hydrothermal system thought to be responsible for the formation of a volcano-hosted, epithermal, now low sulfidation mineral deposit. The system is assumed to be situated on the flanks of a volcanic structure and, therefore, to be supplied by “magmatic” vapors through “dry” degassing, too. Absorption of these vapors into ground water at intermediate depths is likely to lead again to the formation of acid Cl-SO₄ waters, which, on further interaction with rock are converted to neutral Cl waters. Simple gravity separation within the system causes vapors and liquid to be discharged at separate areas. Oxidation of H₂S carried by the vapors gives rise to the production of dilute, acid SO₄ waters, percolating downward to considerable depth, up to 500 m, and the establishment of extensive zones of argillic alteration (Reyes, 1991). The neutral Cl waters may be discharged at lower altitudes considerable distances (10–20 km) away (Giggenbach et al., 1990; Giggenbach and Corrales, 1992). Because of the limited depth, areal extent, and duration of water-rock interaction in these systems, resulting mineral bodies are only of a limited size.

A much more extensive and lasting environment for the extraction of originally magmatic volatiles and metals is provided by the hydrothermal systems associated with formation of “low sulfidation” mineral de-

posits of the porphyry type, as shown in Figure 15. There the penetration of ground water into the cooling rock, a process favored by high hydrostatic pressures and therefore, greater depth, may go on for very long periods, and integrated rock volumes possibly involved in this process may be very large, thus providing a large source of ore-forming components. The cylindrical shape and position of the ore shell at the boundary of potassic to phyllic alteration suggests that the major process giving rise to ore deposition in porphyry metal deposits is cooling and possibly dilution by the incursion of cooler ground water at intermediate depths. Boiling may be more important in low sulfidation, epithermal deposits.

Anyway, if nothing else, my lecture may have provided you with two important criteria to evaluate the geochemical literature on hydrothermal systems: if a paper indiscriminately uses lots of “fluids” beware, if also “f₀₂’s” and “f₂O’s,” read the newspaper instead.

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