

Near-field high temperature transport: evidence from the genesis of the Osamu Utsumi uranium mine, Poços de Caldas alkaline complex, Brazil

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ABSTRACT

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The chemical, isotopic and mineralogical alteration which occurred during primary uranium ore deposition at the breccia pipe-hosted Osamu Utsumi mine, Poços de Caldas, Brazil was studied as a natural analogue for near field radionuclide migration. Chemical and isotopic alteration models were combined with finite difference models of the convective cooling of caldera intrusives. The modeling indicates that the intense chemical, isotopic, and mineralogical alteration of the Osamu Utsumi breccia pipe requires the circulation of $> 10^5$ kg/cm² of boiling hydrothermal fluid $> 200^\circ\text{C}$ through each square centimeter cross-section of the pipe. This circulation could be driven by heat from a 6 km diameter intrusive extending to 10 km depth. Even with this large amount of circulation concentrated in the permeable breccia pipe, uranium solubilities must be $2\frac{1}{2}$ orders of magnitude greater than indicated in the most recent experiments (and more in line with previous estimates) to produce the primary uranium mineralization at the Osamu Utsumi mine.

The same models applied to a hypothetical high temperature waste repository show that heat from radioactive decay will produce a hydrothermal circulation system remarkably similar to that studied at the natural analogue site at Poços de Caldas. The depth of fluid convection induced by the hypothetical repository would be 5 to 10 km, the maximum temperature would be $\sim 300^\circ\text{C}$, the lifetime of the high temperature phase would be a few thousand years, and boiling would occur and cause most of the alteration within the hypothetical waste repository. This physical analysis emphasizes the importance of permeability on a $10 \times 10 \times 10$ km scale in controlling the potential amount of circulation through the hypothetical repository.

Application of the chemical models successfully used to interpret mineralization and alteration at the Poços de Caldas Osamu Utsumi mine to the hypothetical waste repository shows that even in a worst case scenario (waste implaced in a permeable host rock with no measures taken to inhibit flow through the repository) the amount of hydrothermal alteration in the hypothetical repository will be $\sim 0.1\%$ of that in the breccia pipe at Osamu Utsumi. Assuming no barriers to uranium mobility,

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uranium precipitation above the hypothetical repository would be 0.04 ppm (rather than 40 ppm), hydrothermal alteration 0.03 wt% (rather than 30 wt%), etc.

Our analysis indicates that modeled mineralogical alteration is sensitive to the thermodynamic data base used. Prediction of mineralogical alteration (which may be necessary to predict the migration of radionuclides other than uranium, for example) probably cannot be based directly on even very carefully collected laboratory thermodynamic data. Mineralogical complexities of the system, as well as data base uncertainties will require calibration of the thermodynamic framework against mineralogical alteration observed in the laboratory or field.

INTRODUCTION

Uranium was deposited in the breccia pipe that hosts the Osamu Utsumi mine, Poços de Caldas, Brazil, when circulating hydrothermal fluids boiled. The heat that drove the fluid circulation was provided by an episode of lamprophyric ring dike injection and magma intrusion that caused resurgent doming of the Poços de Caldas caldera. The "primary" uranium was subsequently remobilized and concentrated to ore grade by weathering and groundwater infiltration. The weathering and groundwater flow has continued to nearly the present time and provides a natural analogue for certain aspects of the far-field, low temperature migration of radionuclides. This was the main focus of the Poços de Caldas Project. The "hydrothermal" circulation that led to the primary concentration of uranium serves as a natural analogue for certain aspects of the much higher temperature near-field rock alteration that might occur in a waste repository. The analysis of this higher temperature alteration and uranium transport is the subject of this paper.

The intensity of hydrothermal alteration and the mass of uranium transported in both a natural system and a hypothetical waste repository are related to the volume of hydrothermal fluid circulated through the system above some cutoff temperature, which we take here to be 200°C. The amount of fluid circulation at $T > 200^\circ\text{C}$ in a natural system can be estimated from the size of the intrusive and from the intensity of alteration. In this paper we combine physical and chemical models to show quantitatively that a resurgent intrusive body of reasonable size within the Poços de Caldas caldera can circulate the mass of water required to mineralize and chemically and isotopically alter the breccia pipe at the Osamu Utsumi mine as observed. The physical model is then used to analyze the temperature and mass of groundwater that could be circulated through a hypothetical high-level waste repository by the heat generated by the radioactive decay. A "worst case" situation is assumed in which all permeability barriers fail and water is free to circulate through the repository as easily as through the host rock into which it is emplaced. The temperatures attained in the hypothetical repository, the duration of flow through the repository, and the pattern and depth extent of the flow around the repository are all remarkably similar to the natural system at

Poços. Boiling will occur in the hypothetical repository just as it did in the natural system. These similarities allow the intensity of alteration and uranium transport in the hypothetical repository to be estimated by multiplying the intensity of alteration and uranium transport in the Osamu Utsumi mine breccia by the ratio of the mass of fluid hotter than 200°C circulated through the two sites.

All aspects of the natural system are addressed by the physical and chemical analyses. Even though the physical and chemical models we used are simplified in several aspects (e.g. thermodynamic data is estimated where necessary), the result is an overview of the possible behavior of a breached repository over a period of ~10,000 years that shows clearly where data and models need to be improved. This global overview is perhaps the most appropriate contribution a natural analogue can make to issues involving the disposal of high-level waste in a natural environment.

THE NATURAL SYSTEM

Physical aspects

The first step in modeling is to place the mine, where most of our data has been collected, in the context of the full mineralizing system. This is done in Figs. 1 and 2.

Mineralization and alteration in and around the Osamu Utsumi mine occurred 76 million years ago during a pulse of lamprophyric dike injection and resurgent doming of the 30-km wide Poços de Caldas caldera (Schorscher and Shea, 1992; Shea, 1992). The Osamu Utsumi mine is localized in a relatively permeable breccia dike of 0.5 kilometer diameter that lies adjacent to a small syenite intrusive (Fig. 1). The intrusive is probably the apophysis of a larger intrusive at depth. There has been significant erosion since the time of mineralization. Holmes et al. (1992) have estimated erosion rates of 10 to 50 m/Ma over 70 Ma for a total erosion of 0.7 to 3.5 km. Bruno et al. (1992) have pointed out that, taking into account the 30 ppm uranium left behind in the oxidized zone (that will be removed by erosion), the redox front must have migrated at least 0.5 km (and at least this much erosion must have occurred) to produce the uranium enrichment observed at the redox front.

Figure 2 shows a conservative (in the sense that the size of the intrusive is minimized) estimate of what the entire system might have looked like at the time of mineralization. We have assumed a burial depth of 1.5 km and show no surface topography for the caldera walls, etc. It is sobering to realize how little of the system has been sampled from outcrop, mine workings, and drilling (darker area labeled "observations"). This is the first and perhaps most important conclusion to be reached from an attempt at modeling: little is known about the *system* that produced the primary mineralization. It is prob-

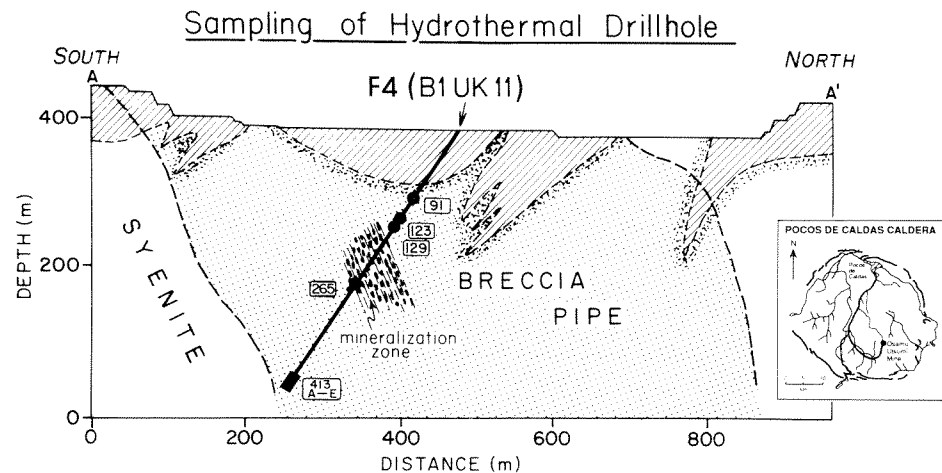


Fig. 1. The Osamu Utsumi mine is located within the ~ 30 km diameter Poços de Caldas caldera which lies about 200 km northwest of Rio de Janeiro. The $N20^\circ E$ cross-section through the mine shows the ~ 500 m diameter breccia pipe that hosts most of the primary uranium mineralization, the hydrothermal drillhole, and the samples from the hole that were petrographically, chemically and isotopically analyzed and are the basis of discussion in this paper. The breccia pipe lies adjacent to a small syenitic stock. The near-surface oxidized zone from which uranium has been leached is hatched. The redox front where this leached uranium is precipitated is shown by the heavy stippling at the bottom fringe of the hatching.

ably unrealistic to expect that the data distribution could ever be expanded sufficiently by deep drilling to provide the constraints we would really like. Fortunately we have quite varied chemical data in the "observation band" of Fig. 2, and this data, when combined with physical and chemical modeling, provides strong constraints on the nature of the entire mineralizing system.

Chemical changes

The reduced portions of the breccia pipe that hosts the Osamu Utsumi mine contain on average about 40 ppm by weight uranium, with local concentrations up to ~ 200 ppm. The hydrothermal fluids that deposited this primary uranium mineralization also affected the whole rock oxygen isotopic signature of the breccia pipe. Its bulk $\delta^{18}O$ composition is quite uniform at $6.6 \pm 0.9\text{‰}$ relative to SMOW. The hydrogen δD compositions of breccia pipe samples show a regular trend (as the intensity of alteration increases) from -82 to -45‰ relative to SMOW. (Shea, 1992). Unaltered syenites in the area have $\delta^{18}O = 8.5 \pm 1.1\text{‰}$ and $\delta D = -80 \pm 10\text{‰}$ (Shea, 1992, Table 1). Thus passage of the hydrothermal solutions through the breccia pipe decreased the $\delta^{18}O$ values of the rocks by a few permil, increased the δD value of the rock, and deposited ~ 40 ppm U. Meteoric water at Poços at the time

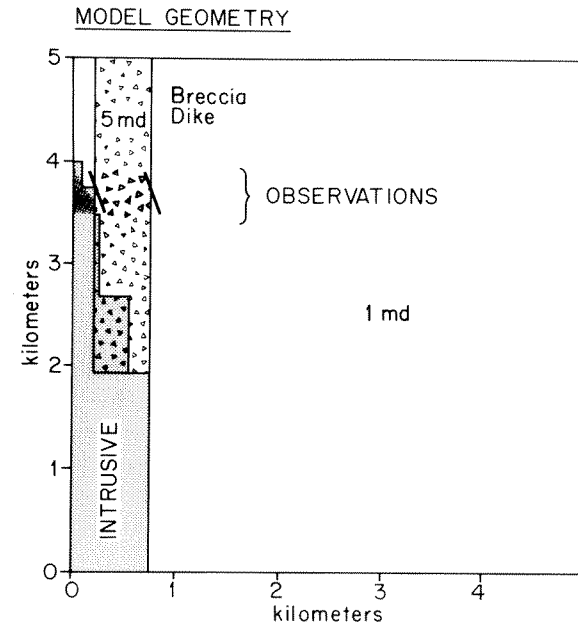


Fig. 2. Hypothetical cross-section of the system responsible for alteration and mineralization at the Osamu Utsumi mine. Observations (from the open pit and drilling) are limited to a thin band ~ 1.5 km below what was the surface at the time of mineralization. The breccia dike is assumed to have a permeability of 5 millidarcies, and the general region a permeability of 1 millidarcy, as indicated.

of mineralization was initially estimated to have had $\delta^{18}O \approx -4\text{‰}$ and $\delta D \approx -20\text{‰}$ (Shea, 1992, Section 3.2). At moderate temperatures the hydrogen isotopic fractionation factor between water and rock is $\sim -30\text{‰}$ (Taylor, 1979). Thus the δD signature of the breccia pipe trends toward values of $\sim -50\text{‰}$ that would be in equilibrium with local meteoric water. There is no indication of a similar shift in $\delta^{18}O$ toward values of $\sim 0\text{‰}$ that would be in equilibrium with local meteoric water at $\sim 200^\circ C$. The $\delta^{18}O$ values cluster around 6.6‰ .

The most striking primary alteration is not isotopic, however, but chemical. Nepheline syenites in the breccia pipe are almost completely stripped of Na, and their K content has been greatly increased. These changes are shown in Table 1 for average values reported in Shea (1992). The change in moles per kilogram between unaltered and altered nepheline syenite is also listed in Table 1.

The chemical changes inferred by comparing equal masses of altered and unaltered rock are subject to several uncertainties, however. The "unaltered" samples may not accurately represent the predecessor of the altered samples. The unaltered samples used in this study are hydrated relative to samples

TABLE 1

Comparison of unaltered nepheline syenites in the Poços Plateau and altered F4 (B1UK11) hydrothermal drillcore at the Osamu Utsumi mine suggests the alteration consists mainly of removal of Na and addition of K. Modal compositions are listed in grams of oxide components per 100 grams of sample in columns 2 and 3. Note $\text{Fe}_2\text{O}_3(\text{tot})$ is total iron reported as Fe_2O_3 . Data are from Schorscher and Shea (1992), Table 3

Mode component	Poços unaltered (4 samples)	Poços Breccia (9 samples)	Chemical change in g/100 g	Alteration in moles of chemical component added per kg rock
Na_2O	7.21	0.62	-6.59	-2.13 (Na)
CaO	1.79	0.83	-0.96	-0.17 (Ca)
MgO	0.37	0.16	-0.21	-0.05 (Mg)
TiO_2	0.78	0.63	-0.15	-0.02 (Ti)
P_2O_5	0.11	0.09	-0.02	-0.003 (P)
$\text{Fe}_2\text{O}_3(\text{tot})$	4.11	4.29	0.18	0.023 (Fe_{tot})
H_2O	2.43	3.02	0.59	0.033 (H_2O)
MnO	0.26	0.57	0.31	0.036 (Mn)
Al_2O_3	19.32	19.57	0.25	0.045 (Al)
CO_2		1.02		
SiO_2	52.53	53.94	1.41	0.23 (SiO_2)
K_2O	7.88	12.95	3.81	0.809 (K)

from the Poços Plateau, for example, and Waber et al. (1992) suggest hydration may be a more important part of the alteration than suggested by Table 1. More importantly, the alteration process may have added (or removed) mass. For example, 70 grams of unaltered predecessor might correspond to 100 grams of altered product, with 30 grams introduced by the hydrothermal solution.

That mass has indeed been added to the unaltered protolith is suggested by the strong correlation between SiO_2 and K_2O in the altered samples. This correlation is pointed out by Waber et al. (1992), and shows unambiguously that SiO_2 is added to the rock during alteration at about twice the rate K_2O is added. The silica addition is not reflected in the equal mass comparisons of Table 1. A more sophisticated analysis is needed.

Such an analysis can be made if at least one of the analyzed components was immobile during alteration and of relatively uniform concentration in the unaltered nepheline syenite. TiO_2 , MgO , and P_2O_5 are all good candidates. We selected TiO_2 and converted the weight percent oxide analyses of the samples from the hydrothermal drillhole shown in Fig. 1 (Table 3 in Schorscher and Shea, 1992) to moles oxide per kilogram rock, and then adjusted the number of moles so that each sample contained the same number (0.076) of moles of TiO_2 . This is a simple form of mass balance or Gresens analysis (e.g. Appleyard, 1980; Babcock, 1973; Gresens, 1967). Regression of the analytical data adjusted in this fashion shows that many of the oxide

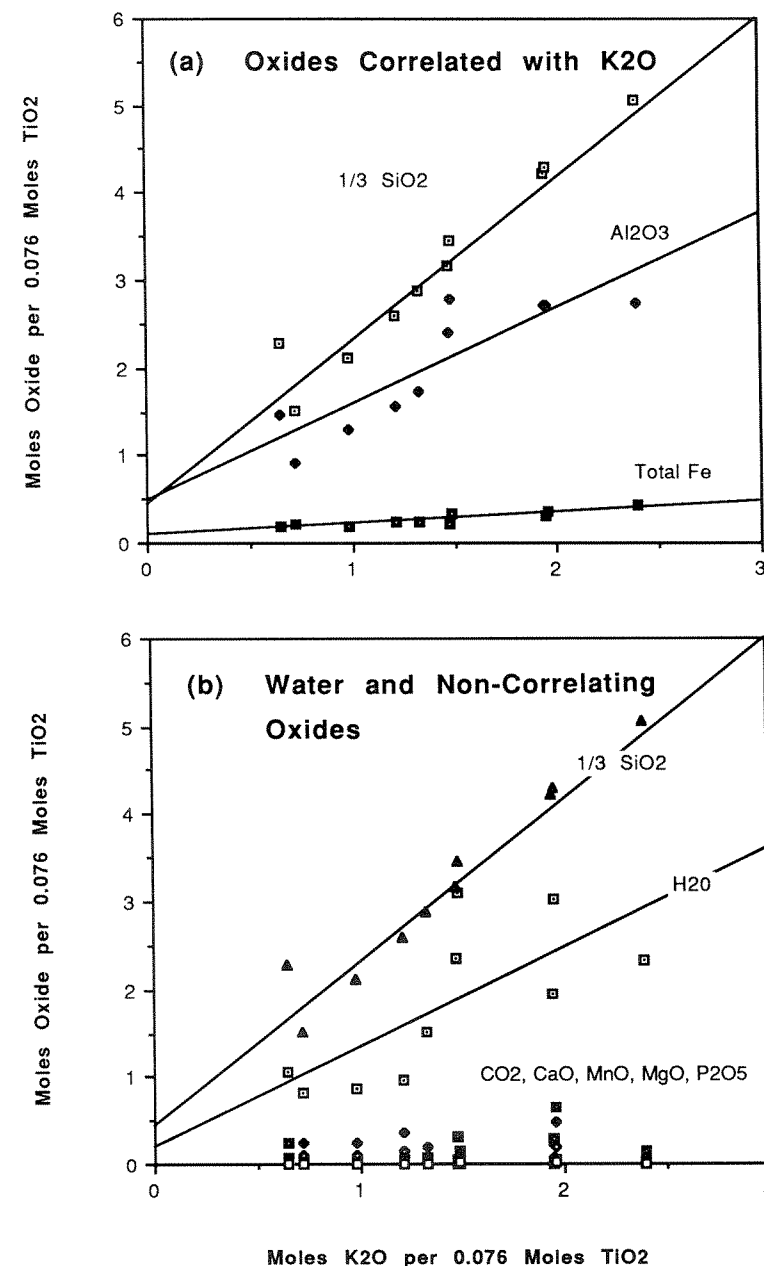


Fig. 3. Regression of oxide rock components against K_2O . Rock compositions were normalized before regression so that all samples contained 0.076 moles of TiO_2 (a simple kind of Gresens correction). Oxide components without regression lines show poor correlation and, within error limits, zero slopes. Data are from Schorscher and Shea (1992), Table 3.

components vary with K_2O but others do not (Fig. 3a, 3b). Without TiO_2 adjustment only SiO_2 varies with K_2O . The greatly increased coherency of the data supports the assumption of TiO_2 immobility.

The following rates of addition (or subtraction) of oxide components relative to K_2O are indicated by the regressions shown in Fig. 3a, b: $SiO_2 = 5.8 \pm 0.5$ moles/mole K_2O (correlation coefficient 0.97), $Al_2O_3 = 1.1 \pm 0.2$ moles/mole K_2O (correlation coefficient 0.87), $Fe_2O_3 = 0.12 \pm 0.02$ moles/mole K_2O (correlation coefficient 0.88), $H_2O = 1.14 \pm 0.38$ moles/mole K_2O (correlation coefficient 0.726), and $CaO = 0.16 \pm 0.11$ moles/mole K_2O (correlation coefficient 0.452). Na_2O dropped very rapidly with alteration. As a consequence Na_2O has a very low and near constant value in nearly all the altered samples. The amount of Na_2O in unaltered Poços Plateau samples suggests the change relative to K_2O was about -2 moles/mole K_2O . All of the other elements have low correlation coefficients (less than 0.31) and slopes equal to zero within error limits.

Thus in a reference frame of a constant number of TiO_2 atoms, an increase of 0.6 moles K_2O (a conservative estimate of the average increase in the Osamu Utsumi breccia) requires a metasomatic flux to the altered rock of 3.46 moles SiO_2 , 1.32 moles Al^{3+} , 0.15 moles Fe, 0.68 moles H_2O , 0.09 moles Ca^{2+} , and -2.4 moles Na^+ .

Petrologic changes

Alteration should also be viewed in mineralogical terms, and the chemical implications of the petrography must be consistent with the changes inferred from the chemical analyses. Petrographic investigations by Schorscher et al. (personal communication, 1989) showed that the alteration in the Poços breccia could be simply viewed as conversion of the original nepheline, sanidine, and aegirine–augite to kaolinite, illite and microcline as indicated in Table 2. The mineral compositions shown in Table 2 have been measured by microprobe (product minerals) or estimated (original minerals).

The fluxes, in moles, of chemical basis species to each kilogram of final altered product that are required to produce the change in mineralogy indicated in Table 2 are shown in Table 3, assuming 100 grams of protolith produces 100 grams of product (column 2), and 70 grams of protolith produces 100 grams of product (column 3). The chemical “basis” species are simply a convenient linearly independent set of chemical components in terms of which the composition of all mineral phases and all solution and gas species can be described. The chemical basis species are usually simple ions, like Na^+ , but are sometimes convenient combinations such as SiO_2 or HS^- . Chemical basis fluxes were calculated by multiplying the stoichiometric matrix which describes the composition of the minerals in Table 2 in terms of the basis species components (see appendix) by the modal mass fractions listed in column 1

TABLE 2

Petrologic alteration of the Poços breccia (F4 drillhole) samples. The minor alteration phases are somewhat arbitrary

<i>Unaltered Poços Plateau nepheline syenites</i>		
30 wt%	Nepheline	$Na_{0.75}K_{0.25}AlSiO_4$
60 wt%	High Sanidine	$K_{0.6}Na_{0.4}AlSi_3O_8$
10 wt%	Aegirine–augite	$NaCa_{0.1}Mg_{0.1}Fe_{0.866}^{3+}Si_2O_6$
<i>Altered Poços breccia</i>		
23 wt%	Illite	$K_{0.3}Mg_{0.05}Fe_{0.125}^{2+}Fe_{0.175}^{3+}Al_{1.8}Si_{3.875}O_{10}(OH)_2$
60 wt%	Max. Microcline	$KAlSi_3O_8$
14 wt%	Kaolinite	$Al_2Si_2O_5(OH)_4$
1 wt%	14Å-Daphnite	$[Fe_2^{3+}Al][AlSi_3O_{10}](OH)_8$
1 wt%	Pyrite	FeS_2
0.5 wt%	Fluorite	CaF
0.5 wt%	Hematite	$Fe_2^{3+}O_3$

TABLE 3

The fluxes of chemical basis species to the rock (in moles per kg rock) required by the mineralogical changes in Table 2, calculated assuming 100 g and 70 g protolith per 100 g of total altered product, are compared to the chemical fluxes estimated by the mass balance (Gresens) analysis discussed in the text

Basis species	100 g protolith for 100 g product	70 g protolith for 100 g product	Fluxes of basis chemical components to rock from mass-balance analysis
Na^+	-2.86	-2.00	~ -2.40
Mg^{2+}	-0.013	-0.000	0
			0 (Ti)
			0 (P)
			0 (Mn)
Ca^{2+}	0.006	0.02	0.09
F^-	0.10	0.10	
Fe_{tot}	0.00	0.12	0.15 (Fe_{tot})
HS^-	0.17	0.17	
K^+	0.50	1.05	
			0.68 (H_2O)
Al^{3+}	0.10	1.38	1.20
$SiO_2(aq)$	0.40	3.26	1.32
			3.46

of Table 2. The moles of each mineral destroyed by alteration are taken to be negative and reduced by the ratio of altered to unaltered rock mass (1 or 0.7).

The last column in Table 3 shows the chemical flux determined from the TiO_2 -constant mass-balance analysis, assuming that the breccia is on average enriched in K^+ by 1.2 moles per kilogram. It can be seen from Table 3 and

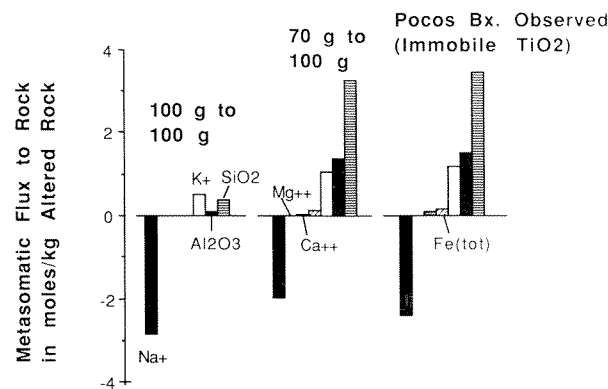


Fig. 4. Petrographic estimates of chemical flux to the rock (in moles per kg of altered rock) are compatible with Gresens analysis estimates ("Observed, immobile TiO₂" subfigure) provided there has been a 30 wt% addition of hydrothermal minerals to the original rock mass.

Fig. 4 that the petrographic observations are compatible with the observed chemical changes provided that the rock mass underwent a net increase of about 30% during hydrothermal alteration. Only in this case will the addition of silica, total iron, and aluminum relative to potassium be compatible with the ratios indicated by the mass-balance analysis.

For about 30 wt% addition of hydrothermal products the chemical and petrologic analyses agree well. The agreement might be improved by changing slightly the amount of minor product phases such as pyrite. The important conclusion to be drawn at this point is that the petrologic observations and observed chemical changes are quite compatible with one another provided the rock mass has been increased by the hydrothermal alteration. Silica, potassium, sulfur and uranium have been added to the rock by hydrothermal fluids, and sodium has been removed. Table 4 shows the basis species flux required to alter a 500 m thick layer of the Poços breccia pipe with density 2.5 g/cc. The hydrothermal system must provide about 432 moles of SiO₂ per cm² cross-sectional area of the breccia pipe, about 150 moles of K and Al per cm², about 0.025 moles/cm² of U, and remove about 300 moles/cm² Na, etc.

Other observations

Fluid inclusions have been observed and studied in fluorite deposited during primary mineralization. These inclusions homogenize at 200–220°C and are of three distinct types. The first two populations have about 10 vol% vapor phase and ~7 wt% salinity (mostly KCl). These inclusions are believed to have been trapped during the early and intermediate stages of alteration. In the third fluid inclusion population, ~90 vol% vapor inclusions coexist with liquid inclusions of high salinity. This mix of vapor- and liquid-domi-

TABLE 4

Estimates of the moles of major constituents deposited or removed by the hydrothermal fluid passing through a 500 m thick section of the Poços breccia pipe at the Osamu Utsumi mine. Additions to the rock are positive and the units are moles per cm² cross-section of the breccia pipe. A breccia density of 2.5 g/cc is assumed

Element	moles/kg breccia added	moles/cm ² in 500 m thick layer of breccia
Na	-2.40	-300
U	2×10^{-4}	0.025
Ca	0.09	11
F	0.10	13
Fe _{tot}	0.15	19
Al	1.2	150
K	1.2	150
SiO ₂	3.46	432

nated inclusions suggests boiling of the warm upwelling solutions and concentration of salts in the residual liquid phase (Waber et al., 1992).

Geological and petrologic studies of the Poços breccia (Schorscher, personal communication, 1989; Waber et al., 1992) indicate the rock alteration occurred in two stages. The first stage, referred to as the "auto-alteration" or deuteric stage, affected the mineralogy but not the bulk chemistry. It occurred between ~700°C (magma temperatures) and ≥350°C. The second, metasomatic, stage of alteration introduced K, S and possibly U, and removed Na. During this stage the rock was ≤350°C. This stage may have been thermally distinct in the sense that it involved heating and then cooling. It could also simply represent the time when circulating fluids first began to significantly interact with the steadily cooling rock mass.

Permeability measurements have been made in a number of drillholes in the area. As reported in the 1986 and 1987 progress reports of the Poços de Caldas project, permeabilities typically decrease from ~10 darcies (10⁻⁴ m s⁻¹) to 10 to 100 millidarcies at depths of a few tens of meters. (See for example measurements in 9-1VC24, 9-1WC11 and a 100 m drillhole in the bottom of the mine open pit.)

FLUID CIRCULATION RESPONSIBLE FOR MINERALIZATION AND ALTERATION

Physical analysis

Taking the above geological, geochemical and geotechnical information into account, calculations have been made of the hydrologic flow that the small intrusive shown in Fig. 2 would produce in an adjacent 500 m wide breccia

pipe extending from the surface to 3 km depth. The permeability of the intrusive (at $T < 300^\circ\text{C}$) and host rock (except the breccia pipe) was taken to be 1 millidarcy. The breccia pipe permeability was 5 millidarcies. The intrusion temperature was 700°C . The intrusion was cooled for 1000 years without any convection (to smooth the intrusive outline and increase computational stability and also to simulate the auto-alteration or deuteric stage of alteration). The permeability of the intrusive was reduced exponentially at temperatures above 300°C as has been indicated to be appropriate by studies of other hydrothermal systems (see Cathles, 1983). This is also in accordance with the temperature ceiling on metamorphic alteration inferred from the studies of petrologic alteration at Poços mentioned above. Free flow was allowed through the top surface. No flow was allowed to cross vertical planes 5 km from the axis of the intrusive and no flow was allowed across the basal boundary which was taken at 5 km depth. The surface pressure (300 bars) was sufficient to prevent boiling in the convective calculations. Boiling was not considered in the physical modeling although it was assumed to occur in the chemical modeling. This inconsistency is not important because we are mainly concerned with estimating the magnitude of fluid circulation in the physical modeling and this is not significantly affected by boiling.

The coupled fluid convection and temperature equations were solved by a Douglas Rachford alternating direction implicit finite difference scheme that is an updated version of that described in detail in Cathles (1977).

The results of the fluid flow calculations are shown in Figs. 5–7. The thermal and convective evolution for the first 10,000 years is shown in Fig. 5. About 2000 years of convection (3000 years elapsed model time) is required for the entire breccia pipe to heat up and for high temperature fluids to reach the surface. Active convection through the breccia pipe occurs from 1000 to 20,000 years. By 20,000 years, however, the intrusive is largely depleted of heat and the lower 2/3 of the breccia pipe is substantially cooled.

Flow is strongly concentrated in the pipe. The integrated fluid mass flux at 10,000 years is shown in Fig. 6. This figure shows that generally the mass flux is less than $\sim 50 \text{ kg/cm}^2$, but in parts of the pipe the integrated flux exceeds 700 kg/cm^2 . The focusing of fluid flow through the pipe is impressive. Figure 7 shows the maximum integrated mass flux as a function of time in the same breccia pipe but with different permeabilities, set in a general 1 millidarcy environment. By the time the intrusive has cooled, up to 2000 kg of hydrothermal solution has passed each cm^2 of cross-sectional area in the high flow portions of the 5 millidarcy pipe. Note, as shown in Fig. 6, that there is a natural tendency for the flow to concentrate in parts of the pipe. This natural tendency would be augmented by any permeability variations within the pipe. Over 1000 kg/cm^2 of hydrothermal fluid can pass through the 5 millidarcy pipe while parts of the system remain hotter than 300°C .

The amount of fluid circulation through the breccia pipe at the Osamu Ut-

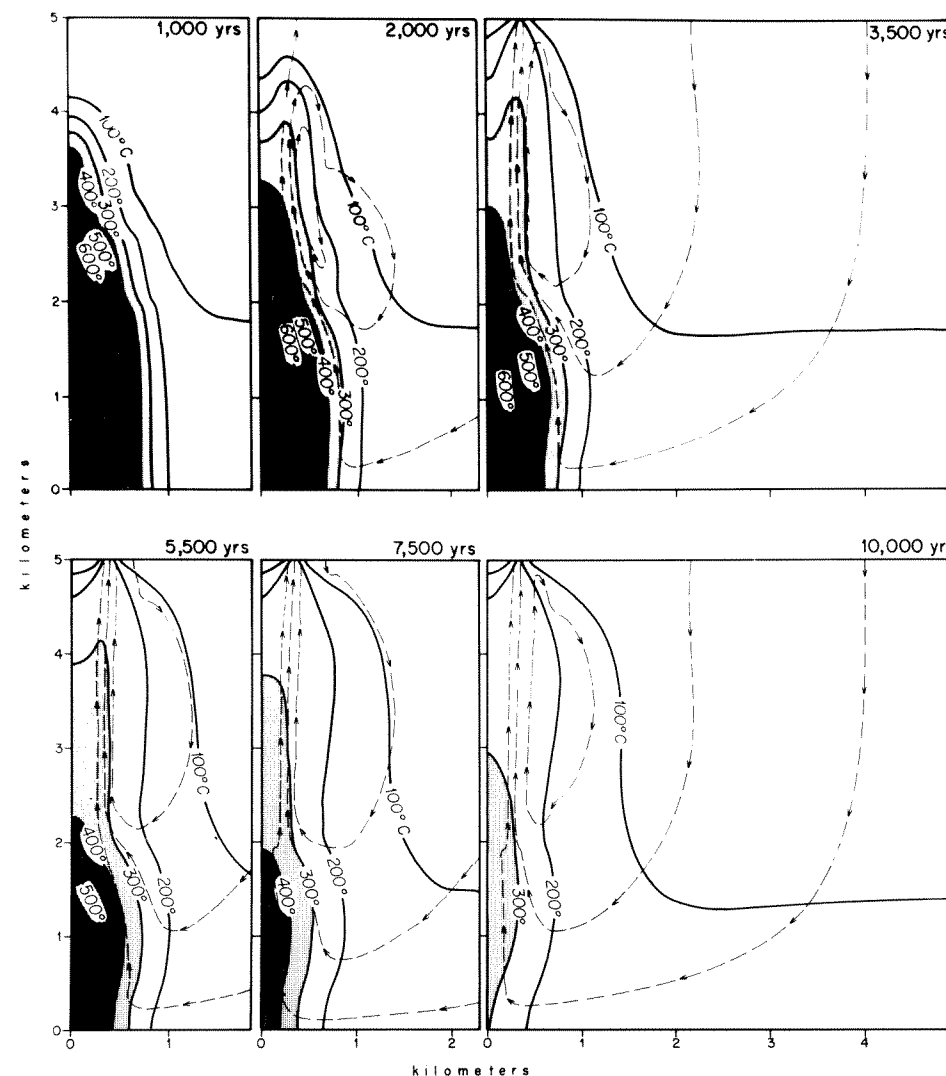


Fig. 5. Cross-sections 1000 to 10,000 years after intrusion showing the progressive cooling of the intrusive depicted in Fig. 2 by pore water convection. The temperature of the initially 700°C intrusive is indicated by solid contours. Streamlines indicating the direction of fluid flow are shown with dashed lines and arrows. The general permeability is 1 millidarcy, except for the breccia pipe which has a permeability of 5 millidarcies, and the intrusive whose permeability decreases exponentially with temperature for temperatures greater than 300°C .

sumi mine depends on many factors. The most important are the size and geometry of the intrusive(s) driving the hydrothermal circulation, and the contrast in permeability between the breccia pipes and the surrounding host. If the size of the intrusive were doubled, twice as much hydrothermal solution

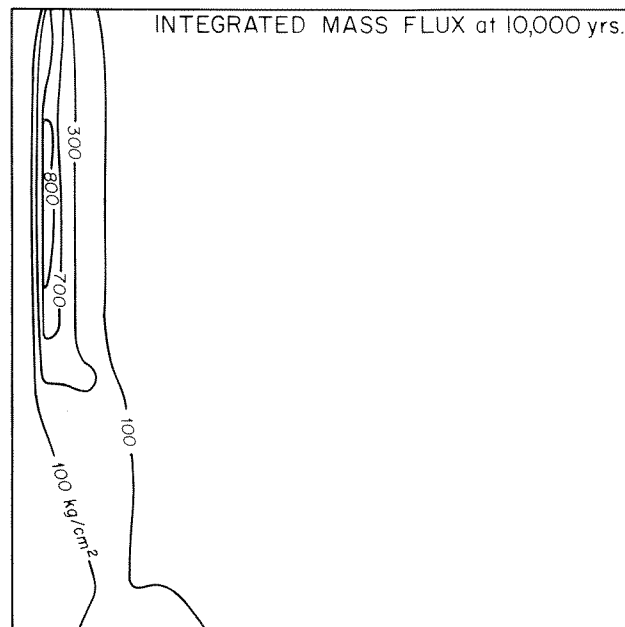


Fig. 6. The total fluid flux after 10,000 years of convective cooling. The inner parts of the breccia pipe have seen the passage of over 800 kilograms of hydrothermal fluid per square centimeter plan cross-section of the pipe.

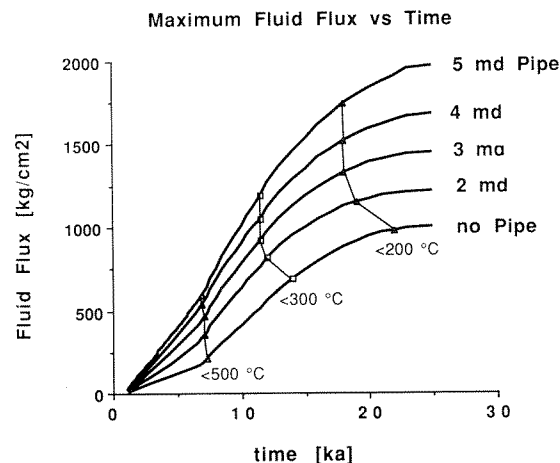


Fig. 7. The maximum integrated fluid flux anywhere in the pipe as a function of time. Convection starts after 1000 years of conductive cooling. Points at which the maximum temperature of the intrusive falls below 500°C, 300°C and 200°C are indicated on each curve.

could circulate through the pipe. If the pipe were more permeable relative to its surroundings, more flow would be attracted to it, and the mass flux would be concentrated in a smaller fraction of the pipe. But beyond a certain point, increasing the pipe permeability will not attract further fluid to the pipe. This is illustrated by Fig. 7 at $t < 9$ ka. At later times convection driven by the natural thermal gradient changes the systematics. At permeabilities greater than 3 millidarcies the Raleigh number exceeds the critical value and free convection is driven by normal crustal heatflow. At $t < 9$ ka this natural convection is not significant and the curves show that a 5 millidarcy pipe concentrates flow to nearly the maximum degree possible in a 1 millidarcy environment. If the permeability of the pipe and its surroundings were increased by the same factor, the mass flux through the pipe would not change, and the intrusive would just cool faster.

Clearly a great many calculations could be presented. The base case model shown in Fig. 2 provides a reasonable context for analyzing the circulation required for mineralization and alteration. We will return to the issue of larger intrusives and greater fluid circulation after analysis of the chemical flow requirements.

Circulation required for protore uranium mineralization

The most obvious question in a study addressing natural radionuclide transport is whether the amount of hydrothermal circulation identified in the physical base model can account for the protore uranium concentration of ~ 50 ppm observed in the Osamu Utsumi breccia pipe.

Estimates of the solubility of uranium in natural, near-neutral hydrothermal solutions differ by many orders of magnitude. On the one hand the EQ3 data base (Wolery, 1983) and experiments by Lemoine, cited in a review by Kertes and Guillaumont (1985), suggest the solubility of uranium (say by dissolution of uraninite) is 8.4 to 21×10^{-5} molal at 300°C, and strongly temperature-dependent. On the other hand the most recently published experimental study (Parks and Pohl, 1988) found the hydrothermal solubility of uraninite to be 3.3×10^{-10} molal and both temperature- and pH-independent (near neutral pH). There is general agreement that the main complex of uranium is $U(OH)_4$, so the difference apparently resides entirely in the dissolution $\log K$ of uranium minerals.

The Lemoine solubilities are quite compatible with the base physical model for fluid flow through the Poços breccia at Osamu Utsumi. The 0.025 moles of uranium contained per square centimeter cross-section through a 500 m mineralized portion of the pipe (Table 4) could be supplied by between 119 and 297 kg of hydrothermal solution if all the uranium were precipitated and the solution were saturated in uranium at 300°C. This is less than the > 1000 kg/cm² of $> 300^\circ\text{C}$ hydrothermal solution the base model suggests passed

through the pipe (Fig. 7). Furthermore, the strong dependence of uranium solubility on temperature indicated by Lemoine's experiments would provide a natural mechanism for uranium precipitation as the solutions cooled moving up the pipe.

On the other hand it is very hard to see how the breccia pipe at Osamu Utsumi could have been mineralized if the Parks and Pohl solubility is appropriate. First, even if all the uranium were somehow precipitated, $\sim 7.5 \times 10^7$ kg/cm² of hydrothermal solution would be required to pass through the breccia pipe. This is ~ 5 orders of magnitude greater than indicated by the base model. Although we might argue that an increase of 2 or 3 orders of magnitude is possible, a 5 order of magnitude increase is not geologically plausible. This will be discussed further below. Second, if there is no dependence of uranium solubility on temperature as indicated by Parks and Pohl, there is a need to identify a mechanism for uranium precipitation in some particular subsurface section of the pipe.

The Poços de Caldas Osamu Utsumi protore mineralization thus suggests that the uranium solubilities indicated by the experiments of Parks and Pohl are too small by several orders of magnitude, and that Lemoine's solubility data may be more appropriate for natural environments.

Circulation required for isotopic alteration

An isotopic alteration model can be superimposed on the fluid and temperature evolution indicated by the base model shown in Figure 5 and the oxygen isotopic alteration of the system predicted. The oxygen isotopic model is described in Cathles (1983) and was calculated here for the whole rock–water fractionation curve shown in Fig. 8. In these models the initial whole rock oxygen isotopic composition was taken to be 10‰ and the local meteoric water entering the top surface -4 ‰. The calculated changes in isotopic value after 10,000 years (9000 years of convective cooling) are shown in Fig. 9.

The evolution of rock oxygen isotopic values follows a similar pattern for all intrusives cooling by convective circulation (Cathles, 1983). At Poços the light alteration prong originating at the deep margin of the intrusive heat source has entered the breccia pipe by 10,000 years. At the level of the Osamu Utsumi mine, however, the oxygen isotopic shift is small. It is about the same after full cooling; in fact the negative isotopic shift is partly erased in the last stages of cooling. Since only a slight negative oxygen isotopic shift is observed in the Poços breccia pipe at Osamu Utsumi, the base physical model is compatible with the observed oxygen isotope alteration.

The oxygen isotopic alteration in the Poços breccia pipe is related to the circulation of water up a steep temperature gradient at the deep margin of the intrusive heat source. The Osamu Utsumi breccia pipe is far downstream from the oxygen isotopic alteration front behind which the isotopic composition of

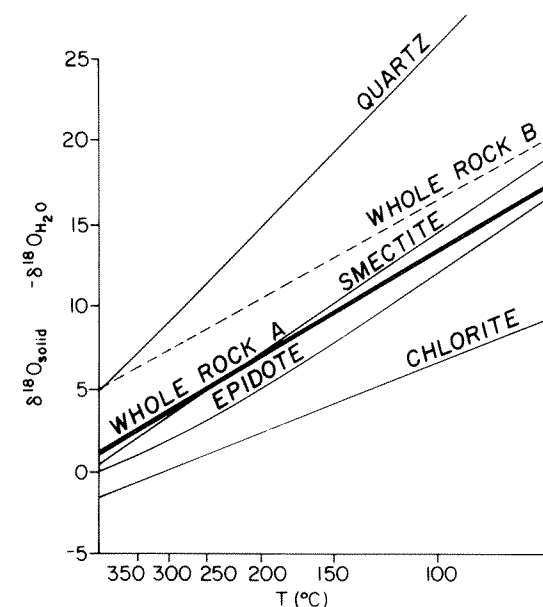


Fig. 8. Oxygen fractionation curves for selected minerals compiled by Cole et al. (1987) are compared to the whole rock fractionation curve used in our modeling (dotted line). The whole rock curve is defined by $1000 \ln a = -3.97 + 2.39 (10^6/T^2)$.

the water reflects its meteoric source. In Fig. 9 the front lies along roughly the 0‰ contour within about 1 km of the surface where recharge is taking place. The fluid passing this front is very close to being in oxygen isotopic equilibrium with the local nepheline syenite and has lost all oxygen isotopic memory of its meteoric source. For this reason the oxygen isotopic alteration in the Poços breccia (the discharge end of the system) is not sensitive to the $\delta^{18}\text{O}$ of the recharge water. Changing the oxygen isotopic ratio of the recharge from the -4 ‰ assumed in the calculations to the -7.5 ‰ measured in the waters of the Osamu Utsumi mine and its immediate vicinity would have no effect on the calculated isotopic alteration in the Osamu Utsumi breccia or at any location past the alteration front.

The change in hydrogen whole rock isotopic values in the pipe is expected to be much more rapid and of a different character than the oxygen isotopic alteration. Hydrogen isotopic alteration has a different character primarily because the meteoric hydrogen isotopic alteration front moves much more rapidly through the system. Water contains 110 moles of hydrogen per kilogram whereas altered Poços de Caldas nepheline syenites contain 2.7 moles of hydrogen per kilogram of rock, and unaltered (unhydrated) nepheline syenite even less. For oxygen the corresponding numbers are 55 and 37. The alteration front moves at a rate directly proportional to the ratio of these two

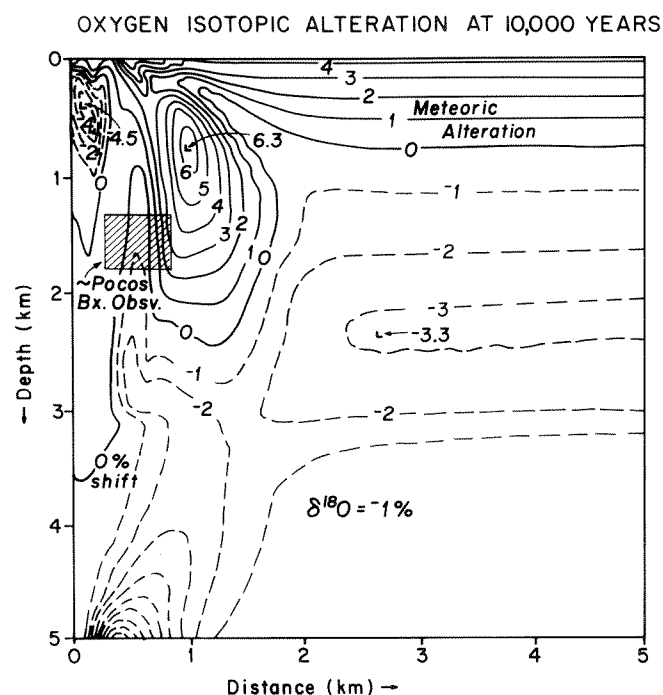


Fig. 9. Shift in whole rock oxygen isotopic signature of the rock caused by the convective circulation of meteoric waters entering the upper left hand surface at -4‰ . The "meteoric alteration" near the surface at inflow areas is the result of light meteoric waters equilibrating with rock at the rate kinetically allowed. Alteration elsewhere is mainly the result of fluids circulating up a temperature gradient as they move to greater depths and as they approach the intrusive (light isotopic shift). Notice that the rocks in the Poços breccia pipe are only very slightly shifted to lighter isotopic signatures, as observed at the Osamu Utsumi mine.

numbers. The alteration front associated with meteoric hydrogen thus sweeps through the convective system ~ 27 times faster than the meteoric oxygen isotopic front. The meteoric hydrogen isotopic front corresponding to the 1 km advance of the meteoric oxygen isotopic front in Fig. 9 would lie 27 km downstream. Since the convective path is less than 15 km, the meteoric hydrogen isotopic front would have swept through the model system in the first 5500 years of circulation. The δD fractionation between rock and water is about -30‰ and relatively independent of temperature (Taylor, 1979; but see also Cole et al., 1987). Thus if the δD of the meteoric water 76 Ma ago at Poços de Caldas were similar to today (-20‰), the rock should show a shift towards δD values of -50‰ from rock signatures of -90‰ . Samples from the drill hole shown in Fig. 1 have whole rock δD values that range from -90 to -45‰ . Furthermore there is an excellent correlation between K_2O alter-

F4 Drillhole Isotopic Analyses

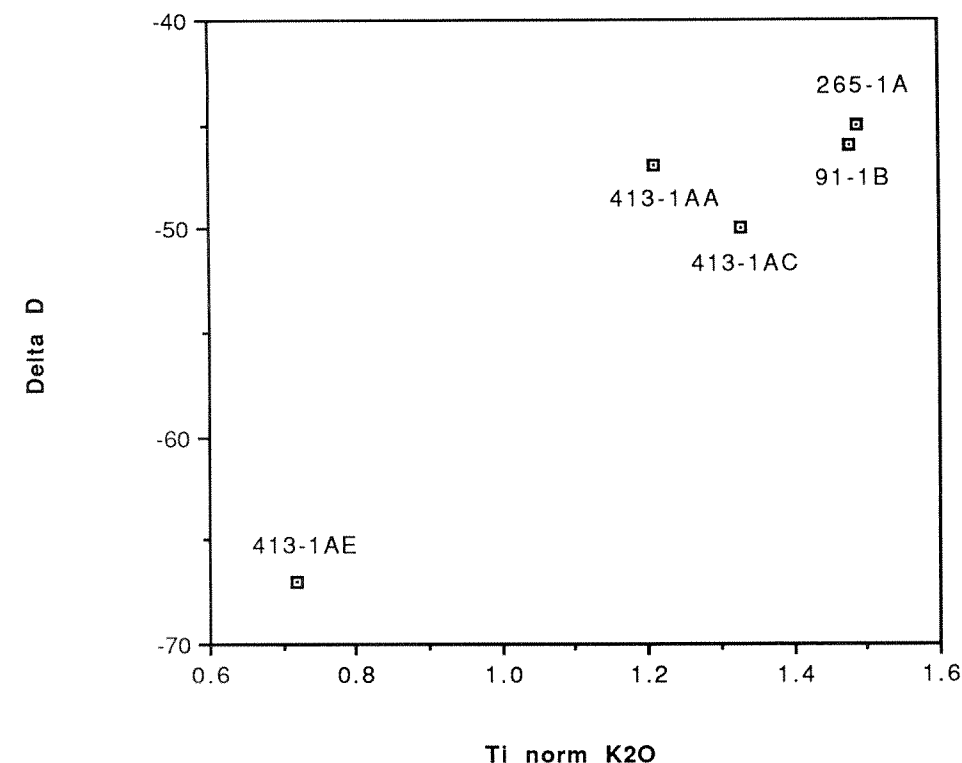


Fig. 10. The whole rock hydrogen alteration of the Poços breccia in samples (see Fig. 3) from the hydrothermal hole at the Osamu Utsumi mine shows an excellent correlation with the intensity of chemical alteration.

ation and δD shown as shown in Fig. 10. This correlation demonstrates that D/H exchange with the host rock took place as alteration occurred.

Circulation required for chemical alteration

Potassium metasomatic enrichment, silicification and uranium deposition are all expected for fluids moving down a temperature gradient (Giggenbach, 1988), since all phases bearing these elements have prograde solubilities. The amount of fluid flow required by the chemical additions indicated in Table 4 can be calculated. These calculations suggest that the alteration requires fluid fluxes considerably greater than indicated by our base physical model.

Silica transport

Because the H_2SiO_3 complex is dominant, silica solubility is dependent only on temperature for waters of slightly alkaline to acid pH near 300°C . Fluids at 300°C in equilibrium with quartz would be ~ 0.01 molal SiO_2 . The silica concentration expected for equilibrium with the aluminosilicates (see Table A-2) in the Poços breccia at Osamu Utsumi is about a half order of magnitude less, or $\sim 3 \times 10^{-3}$. Taking the lower silica solubility, the 420 moles/ cm^2 of silica addition in the breccia pipe (shown in Table 4) would require 140,000 kg of hydrothermal throughput, or a flux about two orders of magnitude greater than indicated in our base model. This is a minimum estimate because it assumes 100% of the silica dissolved at 300°C is precipitated in the 500 m breccia section.

K, Al and Na transport

The fluid flux required to produce the observed potassium, aluminum and fluorine metasomatism and sodium stripping can be evaluated in a fashion analogous to that just employed for silica if the composition of the hydrothermal fluid in equilibrium with altered nepheline syenite can be estimated. Measured solution compositions (say at 300°C and 200°C) from hot springs hosted in nepheline syenites or laboratory experiments could provide the needed fluid composition data directly. Unfortunately, as far as we know, no such analyses have been published. Limited experiments show that hydrothermal waters in chemical equilibrium with undersaturated rocks have higher pH and, as a result, higher aluminum concentrations than hydrothermal fluids in contact with silica saturated rocks (Morey and Fournier, 1961). Aluminum transport is thus expected in alkaline rocks. The solution compositions should be otherwise similar to those in silica-saturated rocks. Magnesium for example should have a very low solubility at hydrothermal temperatures as it does in siliceous rocks (Fournier, personal communication, 1990).

In the absence of laboratory or field solution composition data we must estimate the composition of hydrothermal fluids in equilibrium with nepheline syenite using thermodynamic data. The procedure involves a number of assumptions. Because the solubility of the elements in question depends on pH (and in some cases oxidation state), a full mineral buffer system must be considered. Because a number of the mineral phases buffering the system are not stoichiometrically pure end members, the end member data must be combined to obtain dissolution log K data for the non-end member phases observed at Poços. Aegirine-augite is extremely unstable and alters immediately to a stoichiometrically equivalent variety of riebeckite. We proceed as described in the Appendix by first estimating the thermodynamic data for an appropriate mineral buffer and then "refining" the data so that the calculated solution composition is not too dissimilar to rock-buffered solutions observed in hydrothermal systems hosted by silica-saturated rocks.

The theoretical solution compositions at 300°C and 200°C obtained using the procedures described in Appendix A are shown in Table 5. Only solution species with molalities $> 10^{-5}$ are shown. The solutions have 6477 and 8622 ppm total Cl^- and pH 7.0 and 7.9 respectively. Comparing the 300°C and 200°C columns in Table 5 indicates that SiO_2 , K and Al will tend to be precipitated by solutions cooling from 300°C to 200°C in equilibrium with nepheline syenite, and that there will also be a strong tendency to leach Na.

TABLE 5

Theoretical solution compositions in equilibrium with Poços de Caldas nepheline syenite at 300°C and 200°C . Solution chlorinities are 6477 and 8622 ppm total Cl^- and pH values 7.0 and 7.9 respectively. The partial pressure in bars of a vapor phase in equilibrium with the solutions is also shown

Molal liquid compositions

300°C		200°C	
component	concentration	component	concentration
Na^+	1.28×10^{-1}	Na^+	2.20×10^{-1}
Cl^-	1.27×10^{-1}	Cl^-	2.12×10^{-1}
NaCl	5.48×10^{-2}	NaCl	3.16×10^{-2}
$\text{SiO}_2(\text{aq})$	3.06×10^{-3}	F	6.72×10^{-3}
K^+	2.35×10^{-3}	NaF	1.31×10^{-3}
AlF_4^-	1.09×10^{-3}	$\text{SiO}_2(\text{aq})$	1.24×10^{-3}
F^-	7.39×10^{-4}	OH^-	6.05×10^{-4}
$\text{Al}(\text{OH})_4^-$	7.16×10^{-4}	K^+	4.75×10^{-4}
HF	5.87×10^{-4}	NaSO_4^-	4.55×10^{-4}
KCl	4.33×10^{-4}	HS	4.25×10^{-4}
$\text{H}_2\text{S}(\text{aq})$	4.32×10^{-4}	SO_4^-	3.89×10^{-4}
NaF	2.42×10^{-4}	$\text{Al}(\text{OH})_4^-$	2.05×10^{-4}
AlF_3	1.31×10^{-4}	$\text{H}_2\text{S}(\text{aq})$	5.68×10^{-5}
$\text{H}_2(\text{aq})$	9.09×10^{-5}	H_3SiO_4^-	4.71×10^{-5}
AlF_5^-	8.95×10^{-5}	NaOH	4.14×10^{-5}
OH^-	8.21×10^{-5}	HF	1.11×10^{-5}
HS^-	6.07×10^{-5}		
NaOH	1.21×10^{-5}		

Gas fugacities in bars

gas	300°C	200°C
$\text{O}_2(\text{g})$	4.740×10^{-33}	8.900×10^{-42}
$\text{S}_2(\text{g})$	3.119×10^{-12}	1.535×10^{-15}
$\text{H}_2\text{S}(\text{g})$	1.600×10^{-2}	1.634×10^{-3}
$\text{H}_2(\text{g})$	2.242×10^{-2}	2.181×10^{-3}
steam	66.62	14.05

These chemical changes are in the right direction to explain the metasomatic changes observed in the Osamu Utsumi breccia pipe.

The metasomatic fluxes can be calculated quantitatively. Assuming a system that starts to boil at 350°C, the vertical vapor and liquid flux through the breccia pipe can be calculated assuming no thermal losses and a cold water hydrostatic gradient. These are reasonable assumptions for most hydrothermal systems. If the fluid has an initial chlorinity of 5000 ppm, by the time the 300°C isotherm is reached the mass fraction liquid has been reduced to 0.772 and the chlorinity is 6477 ppm total Cl⁻. At 200°C the mass fraction liquid is 0.58 and the chlorinity 8662 ppm total Cl⁻. The chlorinities of the solutions in Table 5 were chosen so that they correspond to these values. The 300°C and 200°C isotherms in the model hydrothermal system lie at 856 and 156 m depths, and bound a 700 m thick interval of the breccia pipe. The composition of the vapor phase in equilibrium with the hydrothermal fluids in Table 5 can be calculated using the equilibrium constants for gas dissolution in the EQ3 data base (Wolery, 1983). The metasomatic flux of chemical basis species to the breccia pipe between the 300 and 200°C horizons can then be determined by subtracting the chemical basis species flux (represented by the sum of all species in the liquid and gas phases) at 300°C from the flux (in the liquid and gas phases) at 200°C. Details on the method of computation can be found in Cathles (1991) and are also described briefly in the Appendix.

Figure 11 shows the results in terms of the moles of Na, K, Al and SiO₂ added (positive) or removed (negative) by 100,000 kg of boiling hydrothermal solution circulating from 300°C to 200°C through each cm² cross-section of the breccia pipe. These numbers are obtained by multiplying 100,000

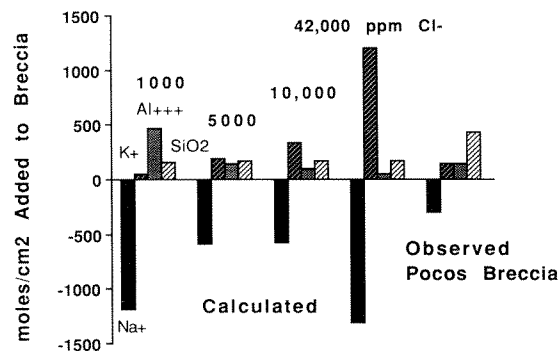


Fig. 11. Comparison of calculated and observed metasomatism in a 500 m interval of the Poços breccia. The metasomatic fluxes to the breccia that result from a 100°C temperature drop from 300°C to 200°C in a boiling system are calculated for different salinity fluids and a 10⁵ kg/cm² fluid flux through the breccia pipe. The liquid phase is assumed to be in equilibrium with the known suite of primary and alteration minerals, and to maintain chemical equilibrium with the vapor phase. The observed metasomatic fluxes (to the rock) are from Table 4.

kg/cm² by the basis species flux to the rock defined above. The mole flux to the rock is directly proportional to the mass of fluid per cm² passed through the pipe. The fluxes are shown for different chlorinity fluids and are compared to the flux inferred from chemical and petrographic observations. The figure shows that changes in pore water and gas composition between 300°C to 200°C can produce the metasomatic alteration observed in the Poços breccia provided ~10⁵ kg of hydrothermal solution circulate through every square centimeter plan cross-section of the pipe. A large fluid throughput is thus required not only by the silica additions, where the thermodynamic data are well known and uncomplicated by mineral interactions, but also by major element fluxes of K, Na and Al.

Some details should be noted in Fig. 11. The intensity of Na depletion is greatest at both low salinities (where pH is highest) and high salinities (where there is more Cl⁻ to charge balance Na⁺). Potassium enrichment increases with salinity, while Al metasomatism decreases (due to changes in pH). Silica metasomatism is independent of salinity. The approximately equal additions of K and Al observed in the Poços breccia are most compatible with cooling of a ~1 wt% (5,000 ppm Cl⁻) solution. This is less than the 7% salinity indicated by fluid inclusions in fluorite.

Petrologic changes

The metasomatic fluxes to the rock indicated in Fig. 11 can be combined with the stoichiometry of the buffer minerals to determine the petrologic changes that correspond to these fluxes. Figure 12 shows that the petrologic changes in the Poços breccia calculated in this fashion are generally similar to those observed. In particular the observed 60 wt% destruction of high sani-

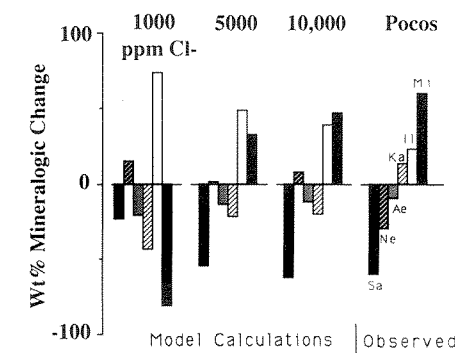


Fig. 12. Comparison of the calculated and observed mineralogical changes (in wt%) in the Poços breccia. Bars represent the wt% change in dissolved and precipitated minerals. Each sums separately to 100%. The calculated alteration is most similar to that observed for fluids with between 5,000 and 10,000 ppm total Cl⁻. Sa=sanidine, Ne=nepheline, Ae=aeirine-augite, Ka=kaolinite, Il=illite and Mi=microcline.

dine, 10 wt% destruction of aegirine, and 60 and 23 wt% deposition of maximum microcline and illite (from Table 2) are simulated well for solutions with salinities around 10,000 ppm Cl^- . Minor phases such as fluorite are also precipitated in a fashion compatible with observations. The calculated destruction of kaolinite and precipitation of nepheline is the opposite of that observed, however. Figures 11 and 12 show that solutions in equilibrium with nepheline syenite circulating down the two phase (boiling) curve could alter the Osamu Utsumi breccia pipe chemically and petrologically as observed.

The modeled mineralogical alteration is extremely sensitive to small changes in the solutions composition at 300°C and 200°C (and to the thermodynamic data that define that composition). This is illustrated in Fig. 13 which shows that changing the dissolution $\log K$ of fluorite by 0.1 log units significantly changes the proportions of alteration minerals. The sensitivity is even greater for riebeckite and is not a computational instability (i.e. is not due to a nearly singular stoichiometric matrix). It is rather a consequence of local equilibrium and fixed mineral composition. Chemical fluxes must be accommodated by stoichiometrically specified mineral phases. In this game of musical chairs, small changes in the chemical flux of certain chemical basis species produce large changes in the percentages of minerals formed. The sensitivity of mineralogical alteration to thermodynamic data might be reduced by a more flexible solid solution accommodation of changes in the chemical flux or kinetic factors. However, it seems unlikely that kinetic modification of the chemical flux to the rock, or solid solution flexibility in accommodating that flux, would eliminate the sensitive dependence of mineralogical changes on the dissolution $\log K$ of critical minerals.

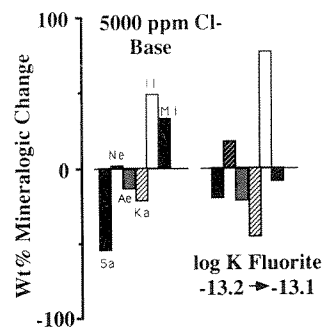


Fig. 13. The calculated mineralogical change is extremely sensitive to the dissolution $\log K$ of certain buffer minerals. This sensitivity is illustrated by comparing the base case mineralogical changes to those calculated for identical cases except for the small changes shown in the dissolution $\log K$ of fluorite. Same conventions as Fig. 12.

Increasing hydrothermal circulation through the Poços breccia at the Osamu Utsumi mine

Both silica and major element alteration require $\sim 10^5 \text{ kg/cm}^2$ of fluid flow through the breccia pipe at the Osamu Utsumi mine. This is $2\frac{1}{2}$ orders of magnitude greater than the amount of 200–300°C fluid vented through the 5 m diameter breccia pipe in the base case model. Rough heat balance calculations show that it is quite feasible to increase the hydrothermal fluid flux through the Poços breccia by the $2\frac{1}{2}$ orders of magnitude, but that much greater increases are implausible. An upper limit is a $3\frac{1}{2}$ order of magnitude increase over the base model. The contribution of magmatic water cannot be significant.

In our model calculations the volumetric heat capacity of nepheline syenite was taken to be $0.54 \text{ cal/cm}^3 \text{ } ^\circ\text{C}$. This was augmented by 30% in the core area of the intrusive to account for latent heat of crystallization. Thus the intrusive (2.12 km^2 in cross-sectional area for the half of the intrusive shown in Fig. 5) could supply $8.9 \times 10^{12} \text{ cal}$ in cooling from 700°C to 100°C. If the heat were carried off by waters that were heated to 350°C after interacting with the intrusive, the intrusive could circulate about $2.55 \times 10^7 \text{ kg}$ of hydrothermal solution, or a volume (at 1 g/cc water density) about 1.2 times larger than the volume of the intrusive and a mass about half of the intrusive. If this hydrothermal solution were vented through dike-like breccia pipes 500 m wide on each side of the intrusive, the average mass flux through each pipe would be $\sim 510 \text{ kg/cm}^2$. This is satisfyingly close to the average which can be inferred from Fig. 7, which indicates, as does Fig. 6, that, during the stages of cooling when portions of the intrusive are still hotter than 300°C, most of the heat is vented through the pipe.

The main ways to increase the hydrothermal flux through the Poços breccia are: (1) putting the problem in a three dimensional rather than two dimensional context, and (2) increasing the depth of hydrothermal water circulation (or the depth extent of the magma chamber from which heat is being extracted). A very water rich intrusive (e.g. Dudas, 1983) might contain 10 wt% volatiles. Thus the magmatic volatiles are less than 20% of meteoric water circulation and cannot significantly increase the amount of hydrothermal solution circulated by the intrusive. Magmatic contributions cannot increase the hydrothermal throughput significantly (see Cathles, 1983).

In three dimensions, a slightly larger intrusive 6 km in diameter lying 3 km below the surface and extending to 10 km depth could reasonably feed 3 breccia pipes 500 m in diameter. Making the same calculation as sketched above shows that the hydrothermal flux through each pipe could be $4 \times 10^4 \text{ kg/cm}^2$, or 1.9 orders of magnitude greater than the base case. This can be increased by 0.3 log units if flow is focused in 50% of the pipe, by 0.25 log units if the intrusive were 4 km in radius rather than 3, and by 0.15 log units if the intrusive extended to 13 km rather than 10 km depth. Cumulatively these reason-

able changes could increase the hydrothermal flux through each breccia pipe by 2.6 orders of magnitude over the base case.

A limit to the increase in hydrothermal flux is provided by assuming an intrusive heat source with a diameter equal to the Poços de Caldas caldera (30 km) extending through a 43 km thick crust (e.g. 40 km in depth extent, 3 km below the surface). If this intrusive heat source fed 500 m diameter breccia pipes on 5 km centers, the hydrothermal flux through each pipe would be 1.9×10^6 kg/cm², an increase of 3.6 orders of magnitude over the base model. This can be considered a generous upper bound on any geologically plausible hydrothermal flux through a breccia pipe such as that at the Osamu Utsumi mine.

It can therefore be concluded that the flux suggested by the chemical alteration of the Poços breccia pipe at the Osamu Utsumi mine is quite reasonable, but indicates a larger intrusive with greater depth extent than our base model (Figs. 2 and 5), and effective flow concentration through the pipe. The 5 order of magnitude increase in hydrothermal throughput required by recent estimates of uranium solubility and the uranium mineralization of the pipe is not geologically reasonable, however. The Poços de Caldas deposit thus suggests that ways must be found to increase the uranium solubility under geological conditions by at least $1\frac{1}{2}$ and probably $2\frac{1}{2}$ orders of magnitude above the recent estimates of Parks and Pohl (1988) if natural examples of mineralization such as Osamu Utsumi are to be understood. In addition, if the solubility of uranium is not temperature-sensitive, a precipitation mechanism must be identified.

A circulation model compatible with all chemical data

In summary, then, the simplest geological scenario that will account for all the chemical and petrologic observations (including the indications of boiling and salinity in fluid inclusions) is that an intrusive 6 km in diameter and 10 km in depth extent lies beneath the Poços de Caldas caldera and circulated hydrothermal fluid through ~3 breccia pipes as it cooled by convective interaction with meteoric water 76 million years ago. Uranium, K, SiO₂, Ca and F were added to the nepheline syenite fragments in the breccia pipes, and Na stripped primarily where the solutions dropped from 300°C to 200°C due to boiling. The throughput of hydrothermal solution required to produce the observed uranium mineralization and chemical rock alteration in the breccia pipe at Osamu Utsumi is ~10⁵ kg through each square centimeter cross-sectional area (in plan view) of the breccia pipe.

Because we have increased the hydrothermal fluid circulation by $2\frac{1}{2}$ orders of magnitude by increasing the mass of the intrusive heat source, the isotopic evolution from the recharge zones will not significantly change from the base model already discussed. For example, the near-surface meteoric alteration

in Fig. 9 will penetrate to greater depths, but only in proportion to the increased depth extent of the intrusive. The oxygen isotopic alteration will be controlled by temperature gradient phenomena associated with hydrothermal interaction with the heat source as before, and hydrogen isotopic alteration will be controlled by the δD of the meteoric water influx to the system as before. In other words all aspects of the chemical and isotopic alteration are compatible with the physical model sketched above, which is a relatively minor modification of our base model. We should note, however, that we have not taken into account the vapor phase effects of boiling on isotopic alteration. The above statement assumes whole rock isotopic alteration is not significantly affected by vapor phase transport.

ANALOGUE PREDICTION OF NEAR-FIELD URANIUM TRANSPORT AND ALTERATION AT A HYPOTHETICAL HIGH-LEVEL WASTE REPOSITORY

Design parameters for a hypothetical underground high-level radioactive waste repository were selected from U.S. DOE (1988). In this design a hypothetical repository of 70,000 metric tonnes uranium would require 18 burial panels. Each panel would be 450 × 900 m in plan dimension emplaced at a depth of 200 to 500 m. In the floor of each panel vertical waste canisters with 0.7 m diameter would be emplaced at 5 m spacing. Each canister would be 3 m long. The 18 panels would cover an area 3 km × 3 km. The heat generation in the paneled area would initially be 0.014 kilowatts per m². The rate of radioactive heat generation would decay with time in a fashion that can be described by the following equation:

$$\frac{\text{heat generation}}{\text{initial heat generation}} = 0.5e^{-t/0.2} + 0.5e^{-t/3}$$

In this equation t is time in thousands of years.

The fluid circulation produced by such a waste repository over its 10,000 year statutory life was calculated using the same techniques used to calculate the flow that led to the mineralization of the Poços breccia pipe. In the calculations a heated layer 200 m thick between 250 and 450 m depth is assumed. The heat generation per unit area given by the above formula was converted to a uniform volumetric heat generation rate throughout the 200 m thick zone. As in the Poços system we allowed no boiling in the fluid flow calculations, although in the real case boiling will certainly occur and is assumed in the chemical calculations. We also assume that the environment of the repository is water-saturated. The amount of fluid circulation and temperature depend on the host permeability. We carried out our calculations assuming a uniform permeability in a 10 km wide and 5 km deep domain around and including the repository. The thermal conductivity of the computational domain was 4.2×10^{-3} cal/cm sec °C.

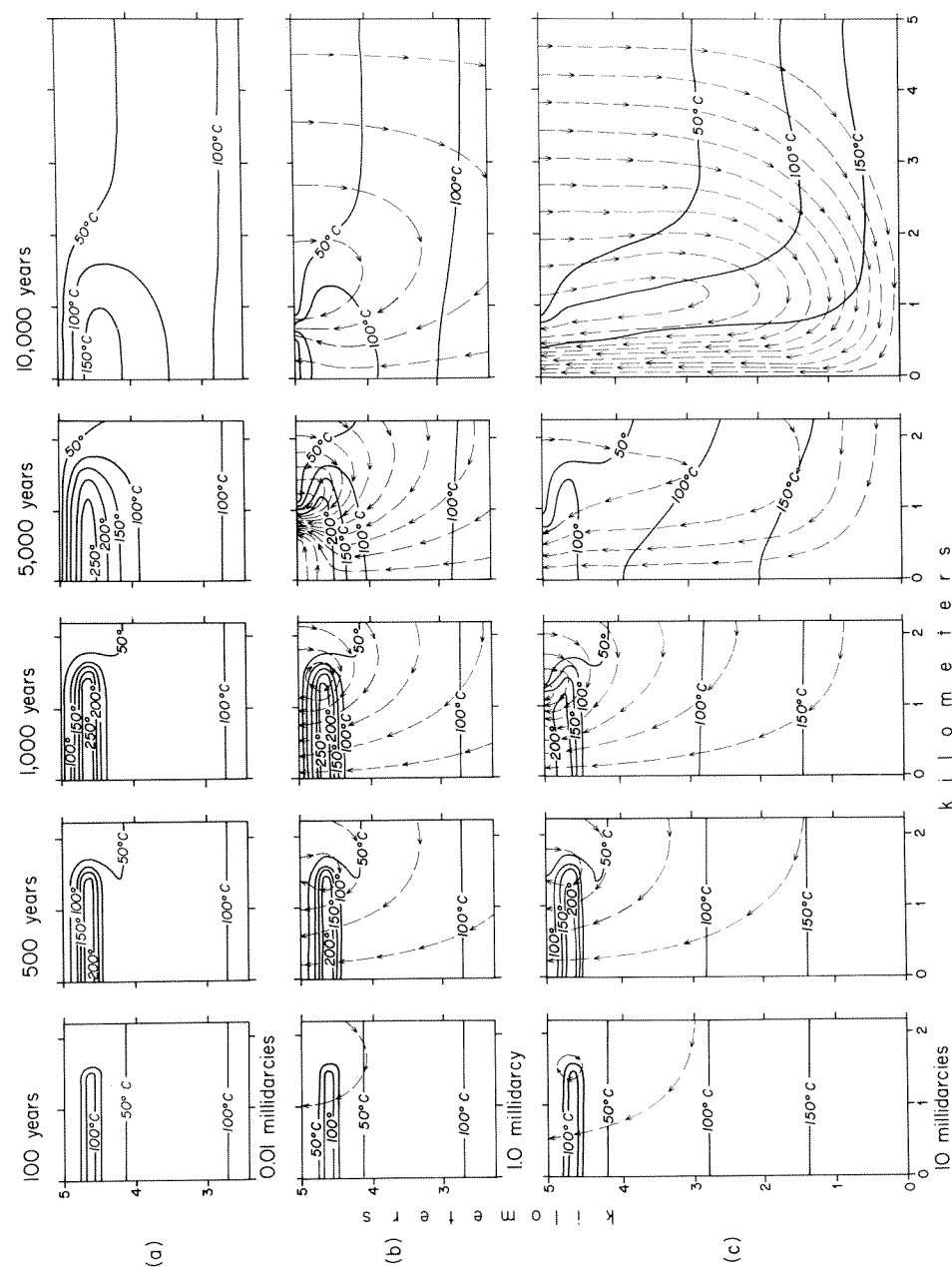


Fig. 14. Calculated temperature and fluid convection around the 70,000 metric tonne high-level nuclear waste repository described in the text. (a) Host is essentially impermeable. Repository reaches temperatures limited only by conduction. (b) Host has permeability of 1 millidarcy, similar to environment at Poços de Caldas. Convection is induced to at least 5 km depth and temperature of repository at any time is reduced. (c) Host has permeability of 10 millidarcies and shows greater convection and more rapid cooling of the repository.

The results are shown in Fig. 14. If the permeability is very low (0.01 millidarcies; Fig 14a), the repository heats up to a maximum temperature of 327°C 2,500 years after burial, and then cools as the radioactive material decays and loses heat generation capacity. If the permeability of the host and repository is 1 millidarcy, substantial convection occurs to ~5 km depth, as shown in Fig. 14b. The repository reaches a maximum temperature of 318°C 2,400 years after waste emplacement. Finally, if the permeability of the repository and its setting is 10 millidarcies, more convection occurs through the repository (Fig. 14c). The waste reaches a maximum temperature of 245°C 900 years after emplacement.

The amount of fluid circulated through the hypothetical repository depends on permeability. For a 10 millidarcy permeability, free (Rayleigh-Bernard) convection is substantial even after radiogenic heat has decayed and is focused on the hypothetical repository by the radiogenic heating. We assume no topography-driven fluid flow, which could change the pattern of convection substantially. Figure 15 shows the maximum cumulative fluid flux above the hypothetical repository for the 1 and 10 millidarcy cases. Figure 15 also indicates the points on the cumulative fluid flux curves where the repository first reaches 200°C and (if applicable) 300°C, and where the repository again cools through these temperatures. The hypothetical repository system will circulate at most about 100 kg/cm² of hydrothermal solution that has interacted with rock hotter than 200°C. Most of the mass flux in the 10 millidarcies case

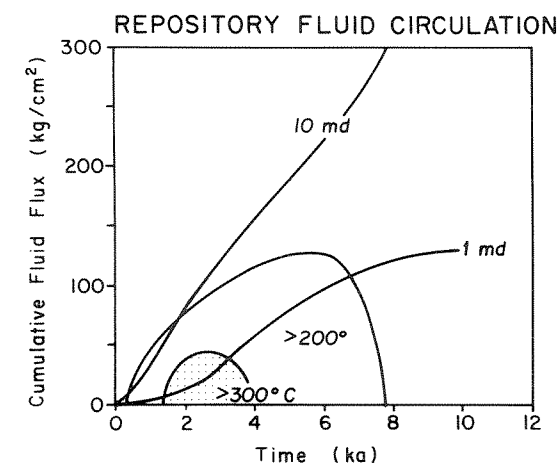


Fig. 15. Cumulative fluid flux for the 1 and 10 millidarcies cases shown in Fig. 14. Points along curves at which the repository first exceeds 200°C and 300°C, and the points at which the maximum temperature again drops below these values, are indicated and contoured. The time-cumulative flux domain where temperatures are greater than 300°C is stippled. This figure shows that less than ~100 kg/cm² of fluids hotter than 200°C will circulate through the repository.

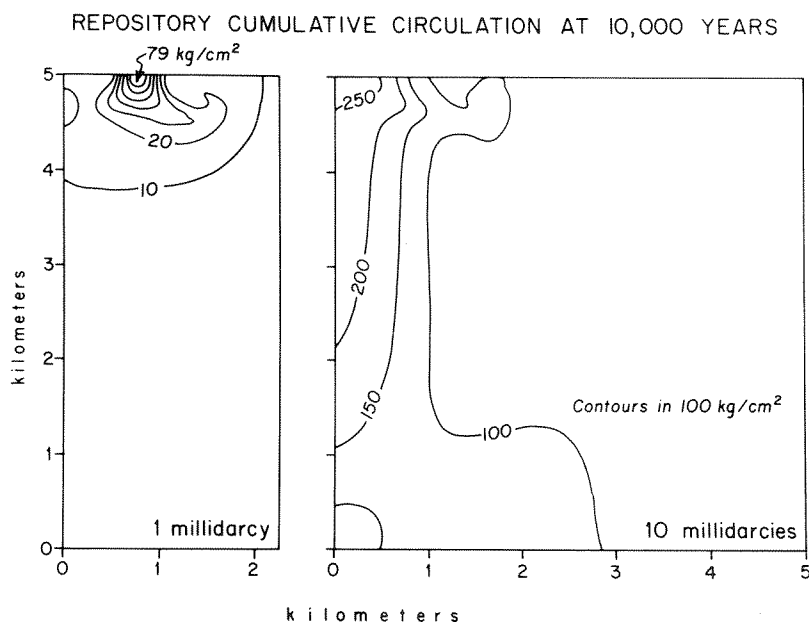


Fig. 16. Cumulative fluid circulation through the hypothetical repository after 10,000 years. Here, as in previous figures, the repository is assumed to have exactly the same permeability as the host into which it is emplaced (e.g. it is assumed no steps are taken to inhibit flow through the repository). The large circulation in the 10 millidarcies case is mostly due to free Raleigh-Bernard convection occurring in the Earth's normal thermal gradient at these high permeabilities. The free convective flow is centered on the hypothetical repository by the radiogenic heating and continues indefinitely, long after the waste has decayed.

occurs after the repository has cooled below 200°C and is associated with natural Raleigh-Bernard convection driven by the normal heat flux from the Earth's interior. This is evident in the pattern of cumulative fluid flux shown in Fig. 16.

Figures 14–16 show that fluid flow in and around a typical high-level waste repository may be strikingly similar to that in the Poços de Caldas analogue. The depth of fluid circulation, the maximum temperatures reached, the thickness of the zone where temperatures will drop from ~300°C to <200°C, and the probability of fluid boiling are all similar. The main difference is that the Poços de Caldas breccia focused flow in a dramatic fashion such that the mineralized parts of that system experienced fluid fluxes of ~10⁵ kg/cm² rather than ~10² kg/cm² calculated for a hypothetical repository emplaced in a region with permeability more than 1 millidarcy. Since chemical transport and alteration depend, all other factors being equal, only on the mass of fluid circulated, the three order of magnitude difference in the mass of fluid circulated indicates that the alteration and uranium enrichment in and above the hypothetical repository will be about 0.1% of that observed in the breccia pipe

at the Osamu Utsumi mine. That is, uranium enrichment in 10,000 years above the hypothetical repository (assuming full waste access and saturation of U in solution) will be on average about 0.04 ppm (vs. 40 ppm in the Poços breccia). The total mass added by alteration will be on average about 0.03 wt% (vs. 30 wt%). The K₂O enrichment (if the host is nepheline syenite) will be on average about 4 × 10⁻³ wt% (vs. the 4 wt% in Table 1). As in the analogue case, the hypothetical repository calculations emphasize the importance of knowing, or at least carefully estimating, the permeability of the whole system (e.g. permeabilities to ~10 km depth, etc). This is particularly important, as Fig. 16 shows, if the permeability of the system is greater than a few millidarcies.

DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

In this paper we have made an attempt to fully analyze the formation of a natural uranium-depositing hydrothermal system and to apply the same methods to uranium transport and alteration in a hypothetical waste repository. We have made a complete (but approximate) analysis of the Osamu Utsumi uranium mineralization located in a 500 m diameter breccia pipe in the 30 km diameter Poços de Caldas caldera, Brazil. Forty ppm U were deposited in a ~500 m interval of the breccia by circulating hydrothermal fluids as they boiled. The fluid circulation intensely altered the breccia, adding about 30 wt% new hydrothermal minerals.

The alteration and uranium mineralization observed in the breccia that hosts the Osamu Utsumi mine require the circulation of a surprisingly large amount of fluid. This is indicated by the amount of silicification and is supported by the removal of Na and the addition of Al and K, and by the fact that the chemical flux produces mineralogical changes closely similar to those observed. Hydrogen and oxygen isotopic alteration in the Osamu Utsumi breccia are also compatible with the total circulation indicated by the alteration. The alteration requires that ~10⁵ kg of hydrothermal solution must have circulated through each cm² cross-section of the breccia pipe. The estimated fluid circulation is conservative (low) because we take a low estimate of the average alteration in the 500 m breccia interval (0.6 moles K₂O / TiO₂ normalized kilogram of rock), and because the altered interval is probably wider than 500 m (400 m is known by mining and drilling, but some of the altered interval has been eroded and drilling has not reached the bottom of alteration). The Poços de Caldas caldera is one of the largest in the world, and a resurgent intrusive of plausible size could easily have circulated the required fluid volume provided fluids circulated to ~10 km depth through rock that had ~1 millidarcy permeability.

The physical model used to analyze circulation through the Osamu Utsumi breccia was then applied to predict the circulation that would be driven by

the heat of radioactive decay from a hypothetical waste repository. The temperatures reached in the repository, the scale of the convective system if the surroundings and repository were permeable, and the mechanisms of alteration and precipitation (steep temperature gradient maintained by boiling in the repository) were all found to be remarkably similar to the Poços system. The main difference between the natural analogue at Poços and the hypothetical repository is that about three orders of magnitude less hydrothermal fluid hotter than 200°C could pass through the hypothetical repository under even the worst of circumstances (complete breach of all permeability barriers such that the repository permeability was the same as the surrounding rock). The estimate of fluid circulation > 200°C through the repository is a maximum estimate. If permeability is at an optimum value the circulation will be this great. If either less or more, the circulation will be reduced. This is because at higher system permeabilities the repository is cooled below 200°C in a shorter time with less total fluid circulation at $T > 200^\circ\text{C}$, while at lower permeabilities the repository remains hotter longer but there is less total flow.

Because the maximum fluid circulation at $T \geq 200^\circ\text{C}$ is 10^3 less than the circulation at Poços, the alteration and radionuclide transport will be at worst less than 0.1% of that encountered in primary (hypothermal) alteration in the breccia pipe at Osamu Utsumi mine. For example, uranium transport will be ~0.04 ppm rather than 40 ppm even if all waste is contacted and leached, and the alteration intensity will be ~0.03 wt% in the completely breached hypothetical repository rather than 30 wt% at Poços. In other words, the hypothetical repository will circulate fluids for as long (~8,000 years) and as broadly (~10 km deep) as the natural system, and both systems will boil near the surface. However, because the radiogenic heat output of the repository is very small compared to the heat output of the intrusive that drove fluid circulation through the Osamu Utsumi breccia in the Poços de Caldas caldera, the repository will not redistribute radionuclides or alter its host environment to anywhere near the degree observed in the Osamu Utsumi breccia.

Apart from the relatively low degree of alteration and uranium transport predicted in the hypothetical breached repository, the most significant conclusion reached by the analogue analysis is the large scale of the fluid circulation, and the indication that further work may be needed on uranium solubilities in the natural environment. Circulation will likely occur in a $10 \times 10 \times 10$ km cube of rock centered on any similar repository. Significant permeability variations (such as might be produced by fractures or permeable strata) within this cube could affect flow through the repository. The uranium solubilities recently summarized by Parks and Pohl (1988) appear to be too small by several orders of magnitude for the natural environment and should be reviewed.

While total mass transport is robust, the calculated mineralogical alteration is sensitive to uncertainties in the thermodynamic data characterizing some

TABLE A-1

Dissolution $\log K$ values at 300°C used to estimate hydrothermal solution composition at Poços. Dissolution was to the basis elements: Al^{3+} , Ca^{2+} , Cl^- , F^- , Fe^{2+} , Fe^{3+} , H^+ , H_2O , HS^- , K^+ , Mg^{2+} , Na^+ and SiO_2 . The mineral dissolution $\log K$ in column 3 are for minerals with the stoichiometry given in Table 2 of the text

Mineral phase	Column 2 End member dissolution $\log K$ (300°C)	Column 3 Dissolution $\log K$ Poços stoichiometry $\log K$ (300°C)	Column 4a and b LogK required for basis activity ratios ~ siliceous rocks	
			300°C	200°C
Nepheline	3.0	2.8	2.84	5.60
Kalsilite	2.1			
High Sanidine	-3.1	-2.8	-2.80	-1.12
High Albite	-2.1			
Aegirine	9.6	-2.1	-3.00	-0.40
Riebeckite	-22.0			
Illite	-5.7	-6.7	-9.00	-5.70
Max.	-3.5	-3.5	-3.50	-2.19
Microcline				
Kaolinite	-5.3	-5.3	-5.26	-1.57
Fluorite	-13.1	-13.1	-13.20	-10.75
Pyrite	-36.4	-36.4	-37.5	-35.62
14Å-Daphnite	8.7	8.7	8.68	20.45
Hematite	-11.3	-11.3	-11.34	-7.87

of the reacting minerals. Trace elements may be incorporated more easily in one mineral phase than another. If these elements are toxic or radioactive it may be important to accurately simulate mineralogical changes in mass transport models. In this case laboratory calibration of the thermodynamic data for the rocks and minerals encountered at a specific site may be necessary.

Flow and chemical alteration have been combined in a simple 300°C–200°C inflow–outflow model. The easiest and most direct way to verify the chemical part of the model and the fluid throughput conclusions that depend on it would be to carry out a set of laboratory experiments to determine the solution composition in equilibrium with Poços de Caldas nepheline syenite at 200°C and 300°C for a range of fluid salinities. The experimental solution compositions would directly verify the solution compositions estimated in Table 5, and could be inverted to verify and refine the dissolution $\log K$ values given in Table A-1. The analysis presented could certainly be refined in many regards. The physical and chemical models should ideally be integrated, rather than just combined.

Any natural analogue analysis is subject to geological uncertainties that can never be completely removed. The geological uncertainties in the present case, however, all appear to be in a direction that strengthens rather than weakens the conclusions reached. For example, flow through the repository is assumed to be uniform. Fluid focusing in fractures of channels could lead to greater alteration in places within the repository, but any flow channeling would likely reduce the total uranium transport since, in our analysis, we have in effect assumed all fluids contact the waste, dissolve, and transport uranium. If flow is diverted by fractures, contact can only be reduced and the total uranium (and other elements) transported to the biosphere will be reduced in proportion to the fraction of channels that contact no waste. It is conceivable (but not likely) that uranium was introduced by much hotter magmatic fluids when the breccia pipe was formed. Such a scenario would again lead to a lower predicted uranium transport in the repository, since the fluids circulating there would then be much cooler than the mineralizing fluids at Poços and hence less capable of transporting silica and uranium. We can find no obvious way that the main conclusions reached in our analysis can be voided by a different geological scenario.

We believe that the interpretation offered in this paper shows the value of analogue studies in assessing radioactive waste isolation designs, and we hope that it will stimulate further work to verify and extend such studies. Such efforts would promote understanding of both mineral deposits and waste repositories.

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APPENDIX. CALCULATION OF SOLUTION COMPOSITIONS IN EQUILIBRIUM WITH NEPHELINE SYENITE AT 300°C AND 200°C

Two mineralogical issues must be addressed before we can calculate the chemistry of waters in equilibrium with altering nepheline syenite.

The *first* is the non-end member stoichiometry of some of the mineral phases summarized in Table 2 in the text. We have handled the observed stoichiometry of nepheline and high sanidine by lever rule interpolation of the dissolution log K data from the end member minerals. For example the dissolution log K of $\text{Na}_{0.75}\text{K}_{0.25}\text{AlSiO}_4$ (Table 2) is obtained by adding 0.75 times the

dissolution log K of nepheline (NaAlSiO_4) of 3.0 and 0.25 times the dissolution log K of kalsilite (KAlSiO_4) of 2.1 to obtain 2.8 as shown in Table A-1. A similar procedure is followed to obtain the dissolution log K of $\text{K}_{0.6}\text{Na}_{0.4}\text{AlSi}_3\text{O}_8$ (Table 2) from high-albite ($\text{NaAlSi}_3\text{O}_8$) and high-sanidine (KAlSi_3O_8). Dissolution log K for the end-member phases are taken from the EQ3 data base (Wolery, 1983).

For the non-end member illite in Table 2 we adjusted the dissolution log K using an oxide component building block approach discussed by Chermak and Rimstedt (1989). Because their convention for expressing mineral free energies of formation from the elements differs from Helgeson's and the EQ3 data base (in taking the elements up to P and T when considering the free energy of formation of minerals and aqueous species), we determined the difference between the free energy of formation of pure end-member illite and illite of the stoichiometry observed at Poços using Rimstedt's approach, and then applied this difference to the free energy of formation of the end member illite in the EQ3 data base. We then calculated the dissolution log K at 300°C and 85.93 bars for dissolution to the basis species of illite of the Poços stoichiometry by subtracting the illite free energy of formation from the sum of the free energies of formation of the basis species into which it dissolves and divided by $-2.303RT$, where R is the gas constant and $T=573.15$ K. The results of the above adjustments are shown in column 3 of Table A-1.

Second, we must address the special problem of aegirine-augite. This pyroxene is extremely unstable in the presence of water at hydrothermal temperatures. It is commonly observed at Poços de Caldas (and elsewhere) with an alteration rim of riebeckite hornblend (a hydrated form of the original mineral). We interpret this as evidence that the outer layers of aegirine-augite at Poços ($\text{NaCa}_{0.1}\text{Mg}_{0.1}\text{Fe}_{0.866}^{3+}\text{Si}_2\text{O}_6$) immediately altered to a variety of stoichiometrically equivalent riebeckite as soon as the augite was exposed to water. This will markedly decrease the dissolution log K of aegirine-augite towards the dissolution log K of riebeckite (with the above stoichiometry) as indicated in Table 5. As an initial approximation we used a shift of -11 log units from 9.6 to -2.1 as also shown in column 3 of Table A-1.

Further changes in the dissolution log K of the buffer minerals are required by the additional requirement that the log activity ratios of the basis species describing the hydrothermal solutions at Poços be not too dissimilar from the ratios commonly encountered in hydrothermal systems in siliceous rocks. These changes are shown by a comparison of columns 3 and 4a in Table A-1. The dissolution log K of aegirine and illite were first adjusted. These changes gave reasonable results except that the flux of HS^- and F^- were much too large. To remedy this the dissolution log K of pyrite and fluorite were adjusted as shown in Table A-1.

Given the dissolution log K for the minerals observed in the Osamu Utsumi breccia at Poços de Caldas, we can solve for the log activity ratios of the basis

species utilizing the Law of Mass Action. The stoichiometric matrix of the mineral phases in Table 2 of the text, S_m , is defined as:

	Al ³⁺	Ca ²⁺	F ⁻	Fe ²⁺	Fe ³⁺	H ⁺	H ₂ O	HS ⁻	K ⁺	Mg ²⁺	Na ⁺	SiO ₂
NEPHELI	1.00	0.00	0.00	0.00	0.00	-4.00	2.00	0.00	0.25	0.00	0.75	1.00
HIGH-SA	1.00	0.00	0.00	0.00	0.00	-4.00	2.00	0.00	0.60	0.00	0.40	3.00
AEGERIN	0.00	0.10	0.00	0.00	0.87	-4.00	2.00	0.00	0.00	0.10	1.00	2.00
MAXIMUM	1.00	0.00	0.00	0.00	0.00	-4.00	2.00	0.00	1.00	0.00	0.00	3.00
ILLITE	1.80	0.00	0.00	0.13	0.15	-6.50	4.25	0.00	0.30	0.05	0.00	3.88
KAOLINI	2.00	0.00	0.00	0.00	0.00	-6.00	5.00	0.00	0.00	0.00	0.00	2.00
FLUORIT	0.00	1.00	2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14Å-DAP	2.00	0.00	0.00	5.00	0.00	-16.00	12.00	0.00	0.00	0.00	0.00	3.00
PYRITE	0.00	0.00	0.00	-1.00	2.00	-2.00	0.00	2.00	0.00	0.00	0.00	0.00
HEMATIT	0.00	0.00	0.00	0.00	2.00	-6.00	3.00	0.00	0.00	0.00	0.00	0.00

The Mass Action Law states:

$$S_m L_{aB} = L_{Km} \quad (A1)$$

where L_{aB} is a column vector of the log activities of the basis species, e.g. a column vector with entries of $\log a_{Al^{3+}}$, $\log a_{Ca^{2+}}$, etc, and L_{Km} is a column vector of the dissolution $\log K$ of the minerals in the Osamu Utsumi breccia listed in Table 2 in the text as listed in columns 3 and 4a and b in Table A-1. The mass action equation may be expressed equivalently by separating the H^+ and H_2O columns:

$$S'_m L_{aB} + S_m^{H^+} L_{aH^+} + S_m^{H_2O} L_{aH_2O} = L_{Km} \quad (A2)$$

where S'_m is the reduced stoichiometric matrix (e.g. the stoichiometric matrix with the H_2O and H^+ columns dropped), $S_m^{H^+}$ is the H^+ column in the stoichiometric matrix, $S_m^{H_2O}$ is the H_2O column, L_{aH^+} is the log activity of H^+ , and L_{aH_2O} is the log activity of water. The log activity of water is usually taken to be zero for dilute solutions, so we may re-express the above equation by setting $L_{aH_2O} = 0$ and multiplying through by the inverse of S'_m :

$$L_{aB} + S_m'^{-1} S_m^{H^+} L_{aH^+} = S_m'^{-1} L_{Km} \quad (A3)$$

The two terms on the left hand side of this equation, when combined, give the log activity ratios of the basis species (the ratio of the basis species divided by the activity of hydrogen ion activity raised to the valence of the basis species). These activity ratios are equal to, and therefore determined by, the right hand side of the equation which is the product of the dissolution $\log K$ of the Osamu Utsumi minerals shown in column 4 of Table A-1 and $S_m'^{-1}$.

Table A-2 shows the log activity ratios of the chemical (basis) species corresponding to the dissolution $\log K$ in Table A-1. Table A-2 also lists typical log activity ratios measured in hydrothermal systems hosted by silica-satu-

TABLE A-2

Log activity ratios of solution basis species in equilibrium at 300°C and 85 bars with mineral phases and $\log K$ data listed in Table A-1

Basis species	Activity ratio	Calculated Poços solution using dissolution $\log K$ from Table A-1		Typical siliceous hydrothermal system
		column 3	column 4a	
Al ³⁺	Al ³⁺ /(H ⁺) ³	-0.12	-0.12	~1.3
Ca ²⁺	Ca ²⁺ /(H ⁺) ²	-29.6	7.5	~8
F ⁻	F ⁻ /H ⁺	8.3	-10.4	
Fe ²⁺	Fe ²⁺ /(H ⁺) ²	3.3	3.3	~3.5
Fe ³⁺	Fe ³⁺ /(H ⁺) ²	-5.7	-5.7	~-6
HS ⁻	HS ⁻ /H ⁺	-10.9	-11.4	
K ⁺	K ⁺ /H ⁺	4.2	4.2	~4
Mg ²⁺	Mg ²⁺ /(H ⁺) ²	49.0	2.8	~5
Na ⁺	Na ⁺ /H ⁺	5.9	5.9	~5
SiO ₂	SiO ₂	-2.5	-2.5	~-2

rated rocks (Typical siliceous column in Table A-2). It can be seen that the relatively small changes in dissolution $\log K$ between column 3 and 4a in Table A-1 produce log activity ratios of Ca^{2+} and Mg^{2+} much closer to the ratios commonly found in siliceous hydrothermal systems.

The log activity of the basis species is determined by eq. (A3) if pH is specified. The log activity of the basis species, together with the dissociation $\log K$ of the aqueous species in the EQ3 data base (see Wolery, 1983), in turn determine the activity (and through the extended Debye-Huckel equation for the activity coefficients the concentration) of all the aqueous species in the EQ3 data base. Charge balance determines pH. Thus the total solution composition buffered by n minerals with distinct composition can be determined. This approach was used to determine the composition of the aqueous solution of various salinities buffered by the Poços minerals at 200°C and 300°C. The method is essentially identical to that used by programs such as EQ3 (Wolery, 1983). The molal concentrations of aqueous species with concentrations $> 10^{-5}$ m in solutions with specified total Cl^- in equilibrium with the minerals are given in Table 2 in the text and the dissolution $\log K$ listed in column 4 of Table A-2 are given in Table 5 in the text.

Once the liquid phase composition and speciation are determined, the composition of a coexisting gas phase can be obtained by application of the $\log K$ for dissolution of various gases. If the vertical flux of heat is constant, and the pressure as a function of depth is defined by the cold water hydrostatic gradient, the fluxes of liquid and vapor are determined as a function of depth. In particular they are known at both the 300°C and 200°C isotherms. The chemical flux in and out of the depth interval defined by these two iso-

therms is thus known and the difference in these fluxes gives the chemical flux to the rock. Chemical and petrologic rock alteration can then be calculated as discussed in the text. Details are given in Cathles (1991).

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