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Isotopic geochemical characterisation of selected nepheline syenites and phonolites from the Poços de Caldas alkaline complex, Minas Gerais, Brazil

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ISOTOPIC GEOCHEMICAL CHARACTERISATION OF SELECTED NEPHELINE SYENITES AND PHONOLITES FROM THE POÇOS DE CALDAS ALKALINE COMPLEX, MINAS GERAIS, BRAZIL

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Isotopic geochemical characterization of selected nepheline syenites and phonolites from the Poços de Caldas alkaline complex, Minas Gerais, Brazil.

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Abstract

This paper presents and discusses the isotopic data from the hydrothermal studies of the Poços de Caldas Natural Analogue Project. The purpose of this study was to elucidate the mass transport of relevant elements and isotopes associated with hydrothermal mineralization and alteration at the Osamu Utsumi uranium mine, particularly as applicable to radwaste isolation concerns in the U.S. nuclear waste program.

Research efforts were focussed on studying the thermal, chemical and hydrologic nature of the palaeohydrothermal regime associated with a breccia pipe at the Osamu Utsumi mine, and related to the geochemical, geochronological and petrological characterization studies of unaltered regional nepheline syenite and phonolite.

The regional rocks studied have a vertically elongated δD, $\delta^{18}O$ *pattern, which possibly indicates meteoric water/rock interaction. Regression of Rb-Sr whole-rock data for the regional nepheline syenite and phonolite samples did not produce isochrons. An internal, mineral separate isochron regression from a nepheline syenite sample, considered representative of unaltered nepheline syenite of the Poços de Caldas plateau, yields an age of 78 Ma, and an initial* $^{87}Sr/^{86}Sr$ *ratio of 0.70511. The moderate initial* $^{87}Sr/^{86}Sr$ *ratios of the regional nepheline syenites are possibly indicative of a mantle source for the alkaline magmatism, with some incorporation of old, high Rb/Sr crustal material. The greater-than-mantle values of* $\delta^{18}O$, *if not due solely to surficial processes, also appear to require some assimilation of crustal material. Sm-Nd data for the regional rocks do not define any isochrons, although the nepheline syenite samples conform very well to a calculated model isochron for 78 Ma and an initial* $^{143}Nd/^{144}Nd$ *of 0.512359. The regional phonolite samples lie markedly off this isochron. This open system behavior is probably due to the phonolite samples having different initial* $^{143}Nd/^{144}Nd$ *values. Even so, all regional samples lie within the "Mantle Array" trend. Their location within the* ϵ_{Nd}-ϵ_{Sr} *space indicates an asthenospheric Mid Ocean Ridge Basalt (MORB)-type source magma*

also contaminated by continental igneous and metamorphic rocks (e.g. the Precambrian schist surrounding the Poços de Caldas plateau).

The rocks studied at the Osamu Utsumi mine from the F4 drillcore have experienced varying degrees of hydrothermal mineralization and metasomatism, and deep weathering. The hydrothermally altered rocks have a quite pronounced δD shift, with only a slight $\delta^{18}O$ *shift.*

The δD-$\delta^{18}O$ *trend of the hydrothermally altered F4 samples most likely reflects the variability of temperature, hydrologic flow and, therefore, water/rock interaction and isotopic exchange in the palaeohydrothermal regime.*

Regression of Rb-Sr whole-rock data for subsamples from a nepheline syenite xenolith sample yields an age of 76 Ma and an initial $^{87}Sr/^{86}Sr$ *ratio of 0.70530. Due to the marked hydrothermal alteration and metasomatism of this sample, the Rb-Sr isotopic system is interpreted as being reequilibrated and thus the regressed age is the age of the hydrothermal event. Using a* $(^{87}Sr/^{86}Sr)_i$ *versus 1/Sr mixing diagram, distinct trends are seen for hydrothermal alteration, mineralization and weathering.*

Again, the nepheline syenite subsamples do not define an Sm-Nd isochron, but conform very well to a calculated model isochron for 78 Ma and an initial $^{143}Nd/^{144}Nd$ *of 0.512365. The Sm-Nd isotopic data also exhibit a likely disturbance by the hydrothermal, metasomatic alteration.*

A lamproite dyke which crosscuts the hydrothermal alteration in the Osamu Utsumi mine gives an age of 76 Ma, which is essentially the same as the Rb-Sr age of the nepheline syenite subsamples.

Zusammenfassung

Dieser Bericht behandelt die Isotopendaten der Untersuchungen über hydrothermale Effekte des natürlichen Analogprojektes von Poços de Caldas. Diese Untersuchung soll den Massentransport geeigneter Elemente und Isotope aufgrund der hydrothermalen Mineralisationen und Veränderungen in der Osamu Utsumi Uranmine erklären, insbesondere im Hinblick auf die Isolation radioaktiven Abfalls im Rahmen des Programms der Vereinigten Staaten für die Beseitigung radioaktiver Abfälle.

Die Untersuchungen konzentrieren sich auf thermische, chemische und hydrologische Eigenschaften des paleohydrothermalen Systems in einer Schlotbrekzie der Osamu Utsumi Mine und wurden mit den geochemischen, geochronologischen und petrologischen Untersuchungen an unveränderten Syeniten und Phonoliten der Region verglichen.

Die untersuchten Gesteine der Region haben ein vertikal verlängertes $\delta D, \delta^{18}O$ *Muster, das möglicherweise auf meteorische Wasser/Gestein-Interaktionen hinweist. Die Regression von Rb-Sr-Daten im Gesamtgestein der Nephelin-Syenit- und Phonolitproben der Region erbrachten keine Isochrone. Eine interne Isochronen-Regression an abgetrennten Mineralien einer Nephelin-Syenitprobe, die das unveränderte Gestein des Poços de Caldas Plateau repräsentieren könnte, lieferte ein Alter von 78 Ma und ein ursprüngliches* $^{87}Sr/^{86}Sr$*-Verhältnis von 0.70511. Solche mässigen* $^{87}Sr/^{86}Sr$*-Verhältnisse deuten möglicherweise auf einen Ursprung des alkalischen Magmatismus im Mantel unter Einschluss von altem Krustenmaterial mit hohen Rb/Sr-Werten. Die Mantelwerte, die* $\delta^{18}O$*-Werte, welche diejenigen im Mantel übersteigen, scheinen, sofern nicht einzig durch Oberflächenvorgänge bedingt, ebenfalls eine Assimilation von Krustengestein zu erfordern. Sm-Nd-Daten für die regionalen Gesteine definieren keine Isochrone, obwohl die Nephelin-Syenitproben sehr gut mit einer berechneten Modell-Isochrone mit 78 Ma und einem anfänglichen* $^{143}Nd/^{144}Nd$*-Wert von 0.512359 übereinstimmen. Die regionalen Phonolitproben weichen deutlich von dieser Isochrone ab. Dieses offene Systemverhalten ist wahrscheinlich darin begründet, dass die Phonolitproben ursprünglich unterschiedliche* $^{143}Nd/ ^{144}Nd$*-Werte aufwiesen. Aber auch so liegen alle Proben der Region im Trend der Mantel-Charakteristik. Die Lage innerhalb des* εNd*-*εSr*-Gebietes deutet auf ein astenosphärisches Quellenmagma vom Typ MORB hin, das auch durch kontinentales erruptives und metamorphes Gestein (z.B. dem präkambrischen Schiefer, der das Poços de Caldas Plateau umgibt) verunreinigt ist.*

Das untersuchte Gestein der Osamu Utsumi Mine vom F4-Bohrkern zeigt unterschiedliche Grade von hydrothermaler Mineralisation und Metasomatose und von tiefer Verwitterung. Das hydrothermal veränderte Gestein hat eine ziemlich deutliche δD-Verschiebung mit einer nur leichten $\delta^{18}O$ Verschiebung.

Die δD-$\delta^{18}O$ Tendenz der veränderten Proben von F4, widerspiegeln höchstwahrscheinlich die Variabilität von Temperatur und Wasserdurchfluss und somit von Wasser/Gestein-Wechselwirkung und Isotopenaustausch im paläohydrothermalen System.

Die Regression von Rb-Sr-Ganzgesteinsdaten für Teilproben einer Nephelin-Syenit-Xenolith-Probe ergibt ein Alter von 76 Ma, und ein ursprüngliches $^{87}Sr/^{86}Sr$ Verhältnis von 0.70530. Aufgrund der deutlichen hydrothermalen und metasomatischen Veränderungen dieser Probe, wird das Rb-Sr-Isotopensystem als wieder ausgeglichen angesehen, woraus folgt, dass das Regressionsalter das Alter des hydrothermalen Ereignisses ist. Anhand eines $(^{87}Sr/^{86}Sr)_i$ gegen 1/Sr Mischdiagrammes sind deutliche Tendenzen für hydrothermale Veränderungen, Mineralisationen und Verwitterung zu erkennen.

Es wird noch einmal darauf hingewiesen, dass die Nephelin-Syenit-Teilproben keine Sm-Nd-Isochrone ergeben, dass sie jedoch sehr gut mit den Berechnungsmodellen für Isochronen von 78 Ma und einem ursprünglichen $^{143}Nd/^{144}Nd$ Wert von 0.512365 übereinstimmen. Die Sm-Nd-Isotopendaten zeigen auch eine wahrscheinliche Störung durch hydrothermale, metasomatische Veränderung.

Ein Lamprotegang, der die Zone der hydrothermalen Veränderung in der Osamu Utsumi Mine durchschneidet, ergibt ein Alter von 76 Ma, also im wesentlichen das gleiche wie das Rb-Sr-Alter der Nephelin-Syenit-Teilproben.

Résumé

On présente et discute les données isotopiques des études hydrothermales du projet d'analogues naturels de Poços de Caldas. L'objectif visé est la compréhension du transport de masse des éléments et isotopes associés à la minéralisation hydrothermale et à l'altération, à la mine d'uranium d'Osamu Utsumi, notamment dans ses aspects applicables à l'isolation des déchets radioactifs dans le cadre du programme des déchets nucléaires aux Etats Unis d'Amérique.

On a focalisé l'étude sur les aspects thermique, chimique et hydrologique du régime paléo-hydrothermal associé à une cheminée bréchique à la mine d'Osamu Utsumi. Ce régime a été étudié en vue de la caractérisation géochimique, géochronologique et pétrographique des néphélines, syénites et phonolites régionales non altérées.

Les roches régionales étudiées présentent une répartition de δD *et* $\delta^{18}O$ *étirée verticalement, indiquant une possible interaction entre la roche et les eaux météoriques. Pour les échantillons de néphéline, syénite et phonolite régionales, les régressions effectuées sur Rb-Sr de la roche totale n'ont pas produit d'isochrones. Une isochrone, obtenue par régression pour un minéral séparé contenu dans un échantillon de syénite néphélitique, a fourni un âge de 78 m.a., et un rapport initial* $^{87}Sr/^{86}Sr$ *de 0.70511. Les rapports initiaux modérés constatés pour* $^{87}Sr/^{86}Sr$ *des syénites néphélitiques régionales indiquent que le magmatisme alcalin provient peut-être du manteau, avec une incorporation de matériaux de la croûte à haut rapport Rb/Sr. Les valeurs de* $\delta^{18}O$ *qui sont plus fortes que celles du manteau, si elles ne sont pas exclusivement dues aux processus de surface, indiquent peut-être aussi une assimilation de matériaux de la croûte. Les données Sm-Nd des roches régionales ne définissent pas d'isochrones, bien que les échantillons de syénite néphélitique sont tout à fait compatibles avec l'isochrone de 78 m.a. et le rapport initial* $^{143}Nd^{144}Nd$ *de 0.512359 calculés par modèle. Les échantillons régionaux de phonolite fournissent des valeurs très nettement en dehors de cette isochrone. Un tel comportement de système ouvert est probablement dû au fait que les échantillons de phonolite possèdent différentes valeurs initiales de* $^{143}Nd^{144}Nd$*. Même dans ce cas, tous les échantillons régionaux se situent dans la tendance du type manteau ("Mantle Array"). Leur localisation dans l'espace* ε_{Nd}-ε_{Sr} *indique un magma source asthénosphérique de type Basalte de crête médio-océanique (MORB en anglais), contaminé par des roches ignées et métamorphiques continentales (par exemple des schistes précambriens entourant le plateau de Poços de Caldas).*

Les carottes provenant du sondage F4 à la mine d'Osamu Utsumi ont subi à des degrés variés une minéralisation hydrothermale et un métasomatisme, ainsi qu'une altération météorique profonde. Les roches affectées par l'hydrothermalisme présentent une dérive assez prononcée pour δD*, et faible seulement pour* $\delta^{18}O$*.*

L'orientation δD*-*$\delta^{18}O$ *des échantillons de roche affectée par l'hydrothermalisme au sondage F4 reflète très probablement la variabilité du régime paléohydrothermal en ce qui concerne les températures et les écoulements souterrains, qui conditionnent l'interaction eau/roche et les échanges isotopiques.*

Les régressions des données Rb-Sr de la roche totale de sous-échantillons de l'échantillon du xénolite de syénite néphélitique fournissent un âge de 76 m.a. et un rapport initial $^{87}Sr/^{86}Sr$ *de 0.70530. En raison d'un hydrothermalisme et d'un métasomatisme marqués, on pense que le système isotopique Rb-Sr de cet échantillon a été rééquilibré, ce qui veut dire que l'âge défini par la régression correspond à l'âge de l'hydrothermalisme. Si l'on utilise un diagramme composé* $(^{87}Sr/^{86}Sr)$ *versus 1/Sr, on peut identifie des directions différentes pour l'altération hydrothermale, la minéralisation et l'altération météorique.*

Là encore, les sous-échantillons de syénite néphélitique ne définissent pas d'isochrone basé sur Sm-Nd, mais sont tout à fait compatibles avec l'isochrone de 78 m.a. et le rapport initial $^{143}Nd/^{144}Nd$ *de 0.512365 calculés par modèle. Les données isotopiques de Sm-Nd révèlent une modification probable par l'altération hydrothermale et métasomatique.*

Un filon de lamproïte, qui recoupe l'altération hydrothermale de la mine d'Osamu Utsumi, fournit un âge de 76 m.a., qui correspond à l'âge Rb-Sr des sous-échantillons de syénite néphélitique.

Preface

The Poços de Caldas Project was designed to study processes occurring in a natural environment which contains many features of relevance for the safety assessment of radioactive waste disposal. The study area, in the State of Minas Gerais, Brazil, is a region of high natural radioactivity associated with volcanic rocks, geothermal springs and uranium ore deposits. It contains two sites of particular interest on which the project work was focussed: the Osamu Utsumi uranium mine and the Morro do Ferro thorium/rare-earth ore body. The first site is notable in particular for the prominent redox fronts contained in the rock, while Morro do Ferro was already well-known as one of the most naturally radioactive locations on the surface of the Earth, owing to the high thorium ore grade and the shallow, localised nature of the deposit.

The features displayed by these two sites presented the opportunity to study a number of issues of concern in repository performance assessment. The four objectives set after the first-year feasibility study were:

1. Testing of equilibrium thermodynamic codes and their associated databases used to evaluate rock/water interactions and solubility/speciation of elements.
2. Determining interactions of natural groundwater colloids with radionuclides and mineral surfaces, with emphasis on their role in radionuclide transport processes.
3. Producing a model of the evolution and movement of redox fronts, with the additional aim of understanding long-term, large-scale movements of trace elements and rare-earths over the front (including, if possible, natural Pu and Tc).
4. Modelling migration of rare-earths (REE) and U-Th series radionuclides during hydrothermal activity similar to that anticipated in the very near-field of some spent-fuel repositories.

The project ran for three and a half years from June 1986 until December 1989 under the joint sponsorship of SKB (Sweden), NAGRA (Switzerland), the Department of the Environment (UK) and the Department of Energy (USA), with considerable support from a number of organisations in Brazil, notably Nuclebrás (now Urânio do Brasil). The first-year feasibility study was followed by two and a half years of data collection and interpretation, focussed on the four objectives above.

This report is one of a series of 15, summarising the technical aspects of the work and presenting the background data. A complete list of reports is given below. Those in series A present data and interpretations of the sites, while those in series B present the results of modelling the data with performance assessment objectives in mind. The main findings of the project are presented in a separate summary (no. 15).

The work presented in this report is a detailed description of rock isotopic systematics from selected unaltered regional rock samples from the Poços de Caldas alkaline complex, with particular reference to objective 4, and provides a regional context for interpretation of the more site-specific studies.

Poços de Caldas Project Report Series

Series A: Data, Descriptive, Interpretation

Report No.	Topic	Authors (Lead in Capitals)
1.	The regional geology, mineralogy and geochemistry of the Poços de Caldas alkaline caldera complex, Minas Gerais, Brazil.	SCHORSCHER, Shea.
2.	Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil. I: Osamu Utsumi uranium mine.	WABER, Schorscher, Peters.
3.	Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil. II: Morro do Ferro.	WABER.
4.	Isotopic geochemical characterization of selected nepheline syenites and phonolites from the Poços de Caldas alkaline complex, Minas Gerais, Brazil.	SHEA.
5.	Geomorphological and hydrogeological features of the Poços de Caldas caldera and the Osamu Utsumi mine and Morro do Ferro analogue study sites, Brazil.	HOLMES, Pitty, Noy.
6.	Chemical and isotopic composition of groundwaters and their seasonal variability at the Osamu Utsumi and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	NORDSTROM, Smellie, Wolf.
7.	Natural radionuclide and stable element studies of rock samples from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	MacKENZIE, Scott, Linsalata, Miekeley, Osmond, Curtis.
8.	Natural series radionuclide and rare-earth element geochemistry of waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	MIEKELEY, Coutinho de Jesus, Porto da Silveira, Linsalata, Morse, Osmond.

Report No.	Topic	Authors (Lead in Capitals)
9.	Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	MIEKELEY, Coutinho de Jesus, Porto da Silveira, Degueldre.
10.	Microbiological analysis at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	WEST, Vialta, McKinley.

Series B: Predictive Modelling and Performance Assessment

11.	Testing of geochemical models in the Poços de Caldas analogue study.	BRUNO, Cross, Eikenberg, McKinley, Read, Sandino, Sellin.
12.	Testing models of redox front migration and geochemistry at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	Ed: McKINLEY, Cross, Haworth, Lichtner, MacKenzie, Moreno, Neretnieks, Nordstrom, Read, Romero, Scott, Sharland, Tweed.
13.	Near-field high-temperature transport: Evidence from the genesis of the Osamu Utsumi uranium mine, Poços de Caldas alkaline complex, Brazil.	CATHLES, Shea.
14.	Geochemical modelling of water-rock interactions at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	NORDSTROM, Puigdomènech, McNutt.

Summary Report

15.	The Poços de Caldas Project: Summary and implications for radioactive waste management.	CHAPMAN, McKinley, Shea, Smellie.

Content

1. Introduction

The Poços de Caldas caldera complex is a ring structure of Mesozoic age comprising a suite of alkaline volcanic and plutonic rocks, generally containing above-background amounts of uranium (U), thorium (Th) and rare-earth elements (REE). The complex initially suffered a regional postmagmatic deuteric alteration resulting in widespread pervasive argillation and zeolitization of the rocks. Some mobilization and concentration of U, Th, and REE also possibly occurred at this stage. This syngenetic alteration was subsequently modified by hydrothermal water/rock interaction of local extent, which led to the formation of several radioactive anomalies of economic importance. Two of these anomalies, the Osamu Utsumi uranium deposit (with subsidiary Th and REE) and the Morro do Ferro thorium and rare-earth deposit (with subsidiary U), and their relationship to the geological evolution of the region, were the main study sites of the Poços de Caldas Project.

This report is part of the presentation and discussion of data from the hydrothermal studies of the Poços de Caldas Natural Analogue Project. The main purpose of these studies was to elucidate the mass transport of relevant elements and isotopes associated with hydrothermal alteration at the Osamu Utsumi uranium mine, as applicable to radwaste isolation. This is particularly relevant to the anticipated elevated-temperature, near-field regime of an underground repository as currently envisaged by the U.S. nuclear waste program.

Towards this goal, efforts were undertaken to discern and delineate elemental mass transport associated with mineralized veinlets within one of the breccia pipes (ore body B) at the Osamu Utsumi mine. Unfortunately, the drillcore (F4) through the breccia pipe did not encounter a suitably defined veinlet. In addition to the attempt to find and study localized mass transport, the mass transport related to the disseminated nature of the primary, hydrothermal mineralization was also studied. Thus, research efforts were made to study the thermal, chemical and hydrologic nature of the palaeohydrothermal regime associated with the drilled breccia pipe.

In order to better understand the effects of the hydrothermal mineralization/ alteration, studies were conducted on related regional rocks within the Poços de Caldas caldera. The studied rocks were selected to be as unaltered as possible, and representative of the nepheline syenite and phonolite found within the caldera. In this report I compare the isotopic geochemical data which characterize the unaltered regional nepheline syenites and phonolites to the similar, though hydrothermally altered, rock found within the Osamu Utsumi mine, in particular the F4 core.

As part of this secondary goal of general characterization, petrographic and geochemical studies were included. Stable isotopic analysis was carried out to discern any water/rock interaction. Radiogenic isotope systematics of Rb-Sr and Sm-Nd were studied to ascertain the undisturbed values for these rocks, to refine and/or confirm previous geochronological studies, and to extract petrogenetic information for the regional Poços de Caldas nepheline syenites and phonolites. These radiogenic isotope studies were particularly important for delineating the timing of the hydrothermal mineralization and elucidating some of the alteration and mass transport.

Hydrothermal alteration is considered here to be an open-system process taking place at moderately high temperatures (100–350°C), with waters almost exclusively of meteoric origin. This is distinct from deuteric alteration which is a closed-system process taking place at magmatic to submagmatic temperatures, with the waters/fluids probably originating from differentiation and out-gassing of the parental rock mass, and can be thought of as "stewing in its own juices."

As discussed in more detail in Cathles and Shea (this report series; Rep. 13), this hydrothermal alteration initiated an intense potassium enrichment/sodium depletion metasomatism. The geology and elemental geochemistry of the Poços de Caldas caldera is discussed in more detail in Schorscher and Shea (this report series; Rep. 1). The geology and geochemistry of the two main study sites, the Osamu Utsumi mine and Morro do Ferro, are discussed in more detail in Waber *et al.* and Waber (this report series; Reps. 2 and 3).

This study represents the first published results from the application of δD, $\delta^{18}O$ and Sm-Nd isotopic systematics on the rocks of the Poços de Caldas plateau and, as far as I know, the first published application of Sm-Nd on nepheline syenites and nepheline phonolites.

2. Analytical methods

2.1. Sample collection and preparation

All regional samples were collected from surface outcrops (except NS-6 which had already been quarried as pavement block) and were selected to be as fresh as possible. Sample sizes ranged from approximately 10–20 kg. The rocks were trimmed, cut and crushed to a coarse gravel size for ease of shipping.

For further chemical analysis, all analyzed samples were powdered using a ceramic ball and mill pulverizer. Mineral separation was carried out using conventional heavy liquid methods on sieve fractions which had been comminuted using ceramic grinding plates.

2.2. H and O isotopic analysis

The hydrogen and oxygen isotope measurements were made using established procedures at Krueger Enterprises, Inc.. All of the results reported here are for whole-rock samples comprised almost totally of silicate minerals.

The hydrogen isotope method used was based upon Savin and Epstein (1970) where hydrogen is liberated as water and H_2 gas from hydroxyl-bearing minerals. Water and H_2 gas are extracted from the whole-rock sample by a vacuum extraction technique. Any evolved H_2 is transformed to water by reaction with copper oxide. All extracted and transformed water is converted to a final H_2 gas for analysis by passage over hot uranium at ~750 °C. The 2σ uncertainties for the whole-rock analyses are ± 2 ‰. Standards used for calibration include various intra-laboratory standards.

The oxygen isotope method used was based upon Clayton and Mayeda (1963) where reaction with BrF_5 is used to evolve O_2 gas from the sample. The reactions were done in nickel vessels heated to ~650°C for >3 hours. The 2σ uncertainties for the whole-rock analyses are ± 0.4 ‰. Standards used for calibration include NBS-28, plus various intra-laboratory standards. Calculated $\delta^{18}O$ values are normalized such that standard values conform with those of Coplen *et al.* (1983).

The hydrogen and oxygen isotope results are reported in conventional δD and $\delta^{18}O$ notation relative to Standard Mean Ocean Water (specifically V-SMOW; V = Vienna).

2.3. Rb-Sr and Sm-Nd isotopic analysis

Rb-Sr and Sm-Nd isotopic analyses were carried out using standard procedures in the Radiogenic Isotopes Laboratories of the Department of Geology and Mineralogy at The Ohio State University. Both whole-rock and mineral separate samples were analyzed for Rb-Sr isotopes; only whole-rock samples were analyzed for Sm-Nd. Isotopic measurements were performed on a Finnigan/MAT 261A multicollector mass spectrometer or, in the case of Rb samples, on a modified Nuclide 12-inch single collector mass spectrometer. Sm was measured by static multicollection. Sr and Nd were measured in a combination of static and dynamic multicollection, so that $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ represent dynamic analyses.

Analysis of interlaboratory standards yields: $^{87}Sr/^{86}Sr = 0.710239 \pm 0.000012$ for National Bureau of Standards (NBS) 987 and $^{143}Nd/^{144}Nd = 0.511850 \pm 0.000007$ for the La Jolla standard. $^{87}Sr/^{86}Sr$ ratios are normalized to $^{86}Sr/^{88}Sr = 0.119400$ and $^{143}Nd/^{144}Nd$ ratios are normalized to $^{146}Nd/^{144}Nd = 0.721900$.

A total-spiking, single dissolution procedure was used, with no solution aliquoting. The isotope dilution uncertainties for this method are: 0.2 % for Sr, Sm, and Nd; 0.5 % for Rb; 0.5 % in $^{87}Rb/^{86}Sr$ and 0.1 % in $^{147}Sm/^{144}Nd$. The total blanks for these procedures were < 800 pg for Sr, < 200 pg for Rb, and < 100 pg for Nd and Sm.

For the calculation of ϵ_{Sr} and ϵ_{Nd} model values, the following "present day bulk-earth" isotopic ratios were used: $^{87}Sr/^{86}Sr = 0.7047$; $^{87}Rb/^{86}Sr = 0.0847$; $^{143}Nd/^{144}Nd = 0.512638$; $^{147}Sm/^{144}Nd = 0.1966$. The decay constants used are $\lambda_{Rb} = 1.42 \times 10^{-11}$ and $\lambda_{Sm} = 6.54 \times 10^{-12}$ $[a^{-1}]$.

2.4. Ar-Ar isotopic analysis

Ar-Ar isotopic analyses were carried out, using standard procedures, in the Radiogenic Isotopes Laboratories of the Department of Geology and Mineralogy at The Ohio State University.

The biotite separates were irradiated for 100 hours in the Ford Nuclear Reactor at the University of Michigan. Argon was extracted in a stepwise fashion for 30 minutes at each temperature and was purified using ZrAl getters. The argon isotopic ratios were measured statically with a 15-cm radius, 60 degree sector mass spectrometer. The fraction of total ^{39}Ar contained in each gas fraction was determined by signal intensities. Apparent K/Ca ratios were calculated and corrections for interfering nuclear reactions and atmospheric Ar were applied.

3. Regional studies

The major emphasis of the Poços de Caldas Project has been to study solute transport processes as evidenced at the two study sites. Morro do Ferro has been studied for the case of hydrologically driven dissolved and/or colloidally suspended mass transport. The

Osamu Utsumi mine has been studied as evidencing hydrologically driven dissolved and/or colloidally suspended mass transport, secondary alteration mass transport, and hydrothermal mass transport.

In order to properly discern and delineate these effects, particularly the secondary and hydrothermal alterations, the Project undertook the study of selected rock from the caldera region which would hopefully not have been affected by these processes. This was important from both a petrological and chemical point of view.

3.1. Geology and petrology

The geology and petrology of the Poços de Caldas region is discussed in more detail in Schorscher and Shea (this report series; Rep. 1). The following is a short summary of geological and petrological particulars which are applicable to subsequent isotopic geochemical discussions.

The Poços de Caldas caldera complex is circular-shaped with a mean diameter of approximately 33 km and is situated about 220 km north of São Paulo, in the state of Minas Gerais, central-eastern Brazil (Fig. 1). The principal rock types of the alkaline complex are subvolcanic phonolites, nepheline syenites, volcanic phonolites, volcanoclastics and eudialyte-bearing nepheline syenites (Ulbrich and Gomes, 1981) (Fig. 2).

The evolutionary history of the Poços de Caldas caldera (modified from Ellert, 1959 and Ellert *et al.*, 1959) involves doming of the Precambrian basement, eruption and deposition of phonolite lavas and volcanoclastics, caldera subsidence, intrusion of nepheline syenites forming ring dykes and minor circular features, and intrusion of eudialyte-bearing nepheline syenites, plus nepheline phonolites.

As noted in Schorscher and Shea (op. cit.), the studied Poços de Caldas regional samples can be divided petrographically into three groups: plutonic nepheline syenite, subvolcanic phonolite and volcanic phonolite. However, these three groups are not clearly distinct elementally or isotopically. Therefore, for clarity of the geochemical discussion in this report, the studied regional rocks have been simplified into two groups: nepheline syenite and nepheline phonolite, following the classification of Streckeisen (1967).

The nepheline syenites and phonolites of the Poços de Caldas region are mineralogically quite complex, but essentially the same in overall composition. Major differences are more of a qualitative than a quantitative mineralogical nature.

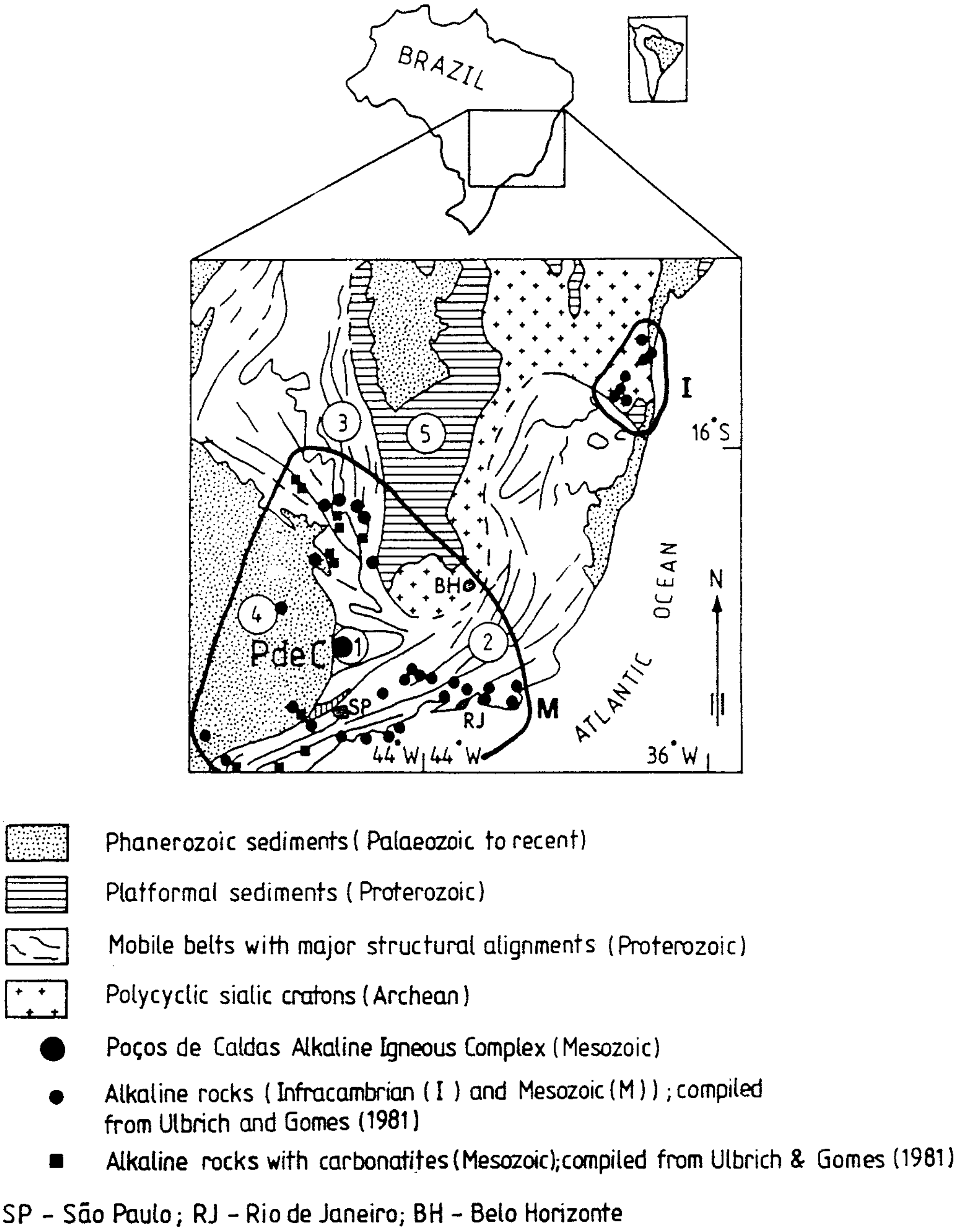

Figure 1. A simplified regional geological map (after Almeida Filho and Paradella, 1977) showing the locations of alkaline rock and the Poços de Caldas complex (the large closed circle symbol). Tectonic subdivisions are: (1) Guaxupé Massif cratonic block (Archean); (2) Ribeira mobile belt (Proterozoic); (3) Brasilia mobile belt (Proterozoic); (4) Paraná Basin sediments and basalts (Phanerozoic) and coastal sediments (Tertiary); (5) São Francisco craton (Archean) with a platformal sediment cover in the west (Proterozoic); closed circles = Mesozoic alkaline rocks (Ulbrich and Gomes, 1981); closed squares = Mesozoic alkaline rocks with carbonatites (Ulbrich and Gomes, 1981).

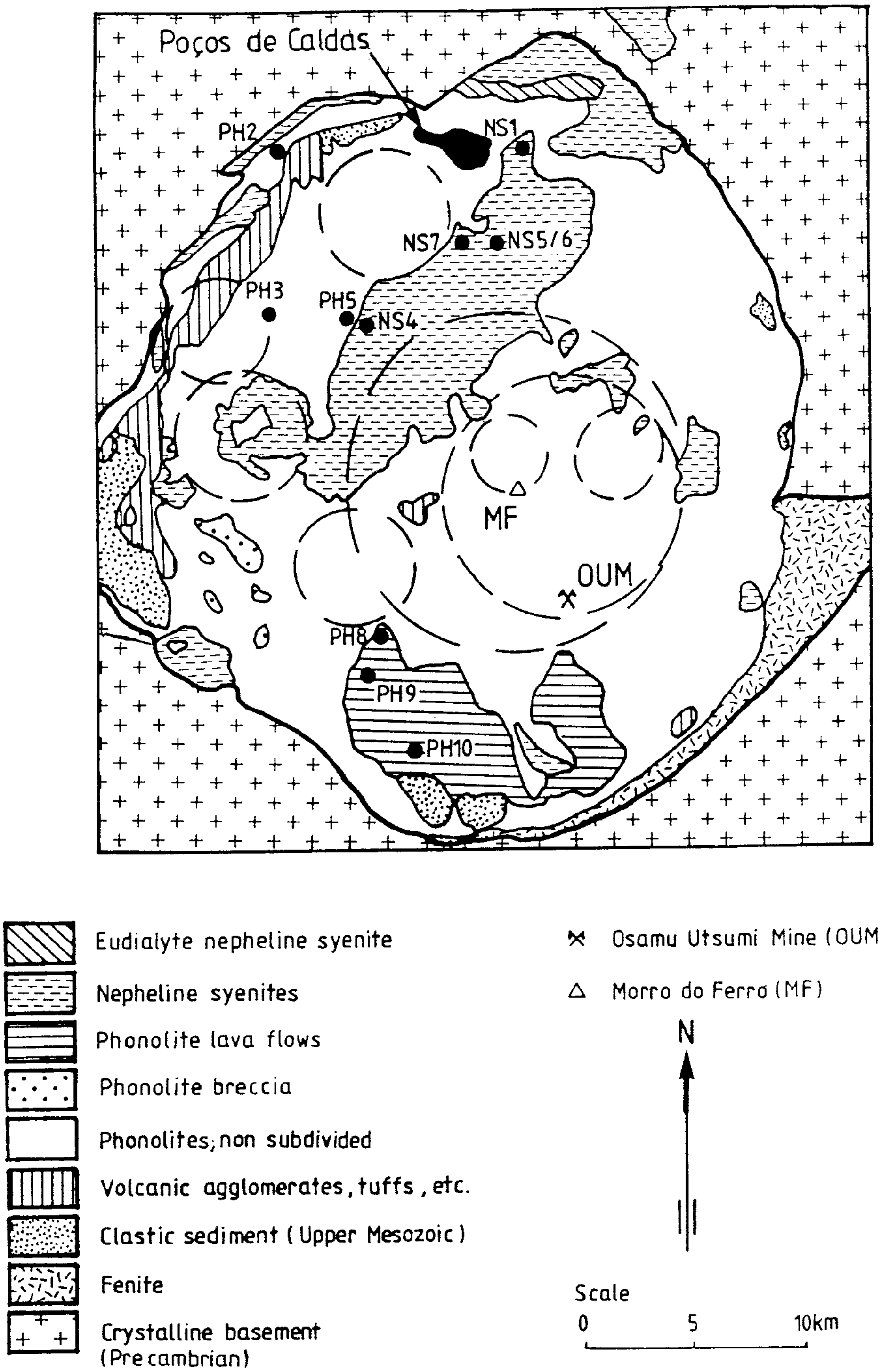

Figure 2. A simplified geological map (after Ellert et al., 1959 and Almeida Filho and Paradella, 1977) of the Poços de Caldas caldera showing the location of all the regional nepheline syenite (NS) and phonolite (PH) samples. Circular features within the caldera are mainly derived from topographic analysis.

The mineralogical data of the nepheline syenites and phonolites are discussed in more detail in Schorscher and Shea (op. cit.).

3.2. Water/rock interaction

One of the important considerations for this study was whether or not the studied regional rocks were affected by water/rock interaction, such as weathering or hydrothermal alteration. The rocks needed to be as unaltered as possible in order to use any analytical information derived from them as a baseline for the studies of the secondary and hydrothermal mass transport studies, especially at the Osamu Utsumi mine.

The $\delta^{18}O$ and δD values for the regional nepheline syenites and phonolites are given in Table I and shown as $\delta^{18}O$ versus δD in Figure 3. The meteoric water line (MWL), also

TABLE I

Stable isotope (δD and $\delta^{18}O$) values for the regional nepheline syenites and phonolites of Poços de Caldas, Brazil.

Sample	δD SMOW[$^0/_{00}$][1]	$\delta^{18}O$ SMOW[$^0/_{00}$][2]
Nepheline syenite		
NS1	-86**	+7.0**
NS4	-90	+8.5
NS6	-74	+9.0
NS7	-68	+9.6
	x = -80(10)	x = 8.5(1.1)
Nepheline phonolite		
PH2A	-93	+7.8
PH2B	-76	+8.7
PH3	-93	+7.2
PH5	-82	+8.1
PH8	-81	+7.2
PH9B	-89	+6.7
	x = -86(7)	x = 7.6(7)

[1] 2σ uncertainties for δD are ± 2 [$^0/_{00}$].

[2] 2σ uncertainties for $\delta^{18}O$ are ± 0.4 [$^0/_{00}$].

**This sample analysis is an average of duplicate analyses on separate aliquots of the same sample.

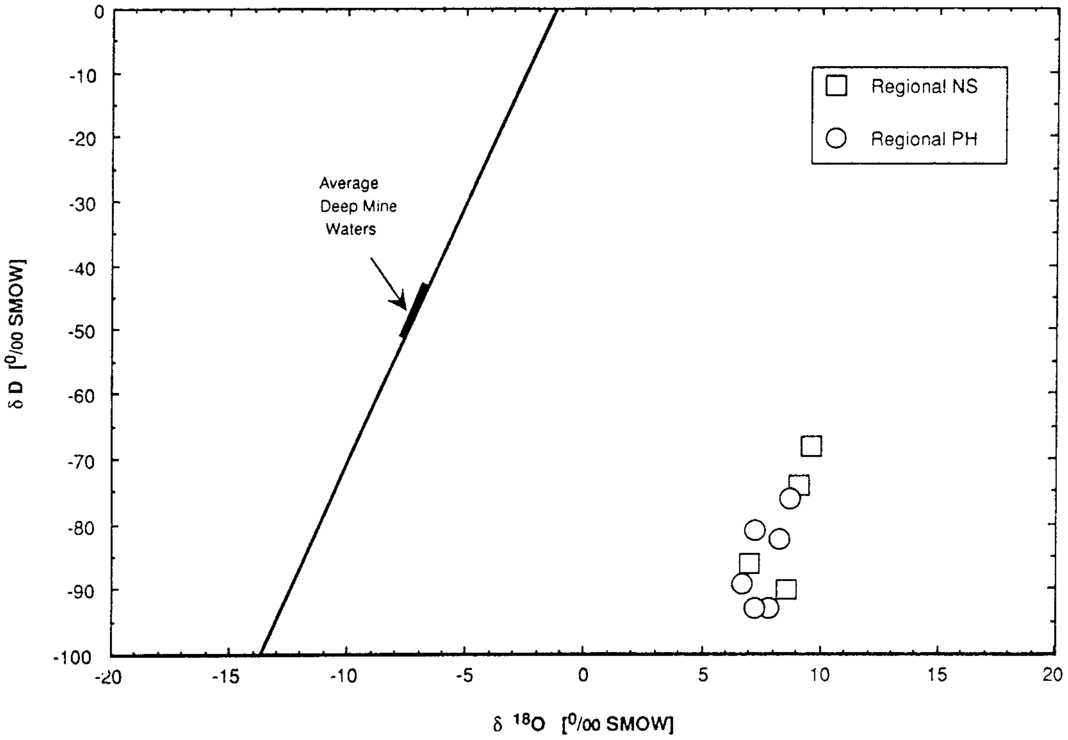

Figure 3. δD and $\delta^{18}O$ values for Poços de Caldas regional nepheline syenite and phonolite plotted relative to the meteoric water line (MWL) δD = 8 $\delta^{18}O$ + 10 of Craig (1961). The average range of deep mine waters lies on the MWL. The marked δD and slight $\delta^{18}O$ shift of the regional rocks, trending up towards the average mine range, is interpreted as representing deuteric and/or post-eruptive incipient meteoric water/rock interaction.

indicated in Figure 3, represents the average trend along which precipitation is found in δD-$\delta^{18}O$ space, and may be expressed as $\delta D = 8\,\delta^{18}O + 10$ (Craig, 1961). Such plotting of the data should help to discern if there are any water/rock interaction effects recorded within the rocks, especially if they have been affected by meteoric water. As will be discussed below, I conclude that the δD – $\delta^{18}O$ values indicate that the regional rocks sampled have possibly experienced slight hydrothermal alteration or weathering.

In order to discern if there is any signature of meteoric water interaction, an estimation of likely meteoric water δD and $\delta^{18}O$ values is needed. For this particular study, both globally estimated and locally measured values are considered.

Sheppard (1986) estimated the global distribution of δD and $\delta^{18}O$, based upon data of Yurtsever and Gat (1981). This distribution was based on data from stations having at least 24 months of record. From their map, one might estimate the $\delta^{18}O$ and δD [SMOW] value for the Poços de Caldas area to be about -4 ± 1 [‰] and -20 ± 10 [‰] respectively. This estimate does not take into consideration the local climate and topographic features that can distort the given large-scale pattern. Given that the Poços de Caldas plateau is a significant topographic high, one might well expect the δD and $\delta^{18}O$ values to be lighter than those estimated from the global pattern of Yurtsever and Gat (1981).

δD and $\delta^{18}O$ values for waters collected in the Osamu Utsumi mine, Morro do Ferro and shallow/surface waters (which are locally acidic) have been determined, and are reported by Nordstrom *et al.* (this report series; Rep. 6). These values range for $\delta^{18}O$ from approximately -8.5 to -5.0 [‰], and for δD from about -55 to -30 [‰]. This range in values can be interpreted as representing seasonal variations in precipitation, since at near-surface temperatures and for relatively short time spans (residence times of tens to hundreds of years) there should be little appreciable water/rock δD and/or $\delta^{18}O$ exchange. Their values on the MWL, shown as a wide bar in Figure 3, probably represent deeper waters that have time-integrated the volume-weighted average value of local precipitation, from which I estimate model values of approximately $\delta D = -50 \pm 5$ and $\delta^{18}O = -7.5 \pm 0.5$. Lacking any additional evidence to the contrary, and to facilitate discussion, I have assumed that the δD and $\delta^{18}O$ local precipitation values are similar to those 76 Ma ago (the estimated age of the hydrothermal (mineralizing) event(s) at Poços de Caldas, see section 4.3).

The range of δD and $\delta^{18}O$ [SMOW] values for the regional nepheline syenites (n=4) varies between -68 and -90 [‰] (average = -80 ± 10) and +7.0 to +9.6 [‰] (average = +8.5 ± 1.1) respectively. The range of δD and $\delta^{18}O$ values for the regional nepheline phonolites (n=6) varies between -76 to -93 [‰] (average = -86 ± 7) and +6.7 to +8.7 [‰] (average = +7.6 ± 0.7) respectively. The vertical elongation pattern of these groups, at the chosen scale, possibly exhibits effects of meteoric water/rock interaction. If extensive water/rock interaction had taken place, these groups would likely be seen to extend and align themselves with the local meteoric water δD value (Blattner, 1985) with some separation due to fractionation. As will be discussed later, the nepheline syenite samples from the F4 borehole of the Osamu Utsumi mine exhibit such a continuation trend away from the unaltered regional group up towards the meteoric δD value.

3.3. Geochronology

3.3.1. Previous studies

Rocks of the Poços de Caldas plateau have been investigated geochronologically using K-Ar and Rb-Sr isotopic methods to determine ages of rock formation in two previous studies. It was hoped that the present study would be able to improve upon and/or confirm the results of these previous endeavors.

Amaral *et al.* (1967) and Bushee (1971) were the first to date the rocks of the Poços de Caldas plateau. They used the K-Ar technique to date 21 samples of whole-rock, feldspar, and biotite and they obtained a range of ages which, they felt, expressed the span of igneous activity of the plateau. Age uncertainties were not included.

Igneous activity was thought to have begun with the eruption of ankaratrite, or olivine-bearing nephelinite, approximately 87.1 Ma ago (n=1). They observed that this event was followed by the eruption of much more voluminous nepheline phonolite around 80 to 81 Ma ago (n=2); this age is also reflected in their earliest nepheline syenite sample (approximately 80.5 Ma). They found that the bulk of the nepheline phonolite was likely emplaced 72 to 76 Ma ago (n=8), although a sample as young as 64 Ma (n=1) was also dated. They observed a clustering of ages (n=3) for the large central nepheline syenite stocks between 60 to 64 Ma ago. A nepheline phonolite dyke which crosscuts nepheline syenite yielded an age of approximately 52.9 Ma (n=1).

The ages determined in the above study, using the K-Ar technique, were an important first step in determining the geochronology of the Poços de Caldas plateau. However, I believe that a number of these K-Ar ages are suspect because the rocks have likely been disturbed by postmagmatic events, such as hydrothermal alteration, contact/regional metamorphism, and/or deep surficial weathering. In particular, the ages determined for the central nepheline syenite in the above studies are significantly younger than those obtained by Kawashita *et al.* (1984) and the present study, using the Rb-Sr technique (which is much less susceptible to postmagmatic disturbance). This decrease in apparent age may be due to ^{40}Ar loss, possibly during hydrothermal alteration and/or deep surficial weathering. It is also possible that this decrease in apparent age is due to an increase in ^{40}K. The nepheline phonolites and nepheline syenites of the Poços de Caldas plateau are now known to have experienced varying degrees of marked potassium enrichment, which should have caused a concomitant enrichment in their ^{40}K isotopic value.

The dating of dyke rocks can be fraught with difficulty because of open isotopic systematics and difficulty in assessing a representative age. Therefore, the age determined for the nepheline phonolite dyke may also be too young. I have not dated any similar material in this study.

In conclusion, I would restrict the span of igneous activity, with a re-evaluation of the above K-Ar data, to range from no more than approximately 72-82 Ma ago, and possibly even less. This position is also taken by Ulbrich (1985), who felt that the interval of caldera activity may even be as short as 1-2 Ma. It should also be noted that the ages determined by the above workers used an older set of constants (Wetherill, 1966), which have subsequently been revised (Steiger and Jäger, 1977). Recalculating would yield ages approximately 2.5% younger than those using the previous K-Ar constants.

Kawashita *et al.* (1984) report Rb-Sr ages for three rock types of the Poços de Caldas plateau. These are: (1) a small, elongate body ($\leq$ 0.5 km by $\leq$ 5 km) of fluorite-bearing nepheline syenite found in the north-eastern part of the plateau; (2) a relatively small (roughly 1 km by 10 km) collection of eudialyte-bearing nepheline syenite bodies, some with a gneissic texture (their chibinite and lujaurite); and (3) the relatively large (approximately 5 km by 20 km) nepheline syenite body found in the central portion of the plateau (their Pedreira nepheline syenite). They report the following ages and initial ^{87}Sr/^{86}Sr values for the three rock bodies, respectively: 1) 89.8(2.8) Ma; 0.7050(1), 2) 86.3(6.0) Ma; 0.7052(1) and 3) 85.0(5.0) Ma; 0.70443(34) and 0.70499(15). It is not apparent from the above abstract whether or not the above ages are whole-rock or internal isochrons, how many samples were analyzed and/or used, or where the samples were collected. No isochron regression parameters are given.

The initial ^{87}Sr/^{86}Sr values reported by Kawashita *et al.* (1984) for the central nepheline syenite, although understandably less precise than the one I calculate, do agree with my model value of 0.70511(1), signifying that the Poços de Caldas nepheline syenite reflects a primitive geochemical source; one of their values of 0.70499(15) numerically concurs with mine within their stated uncertainty range. Their reported values for the other two rock types they studied also concur with my value within their stated uncertainty ranges.

It is of interest to note that the ages of Kawashita *et al.* (1984) tend to support the relatively old ages for peripheral rocks of the plateau, as found for the olivine-bearing nephelinite of Amaral *et al.* (1967) and Bushee (1971), tending towards ages of approximately 87-90 Ma ago. Since I did not sample these rock types, I am unable to corroborate these findings, although, as mentioned above, these ages may be erroneously old.

3.3.2. Current studies

In general, nepheline syenite and nepheline phonolite are the two main rock types present within the Poços de Caldas plateau. The dating and isotopic characterization of regional nepheline syenite which would be comparable to that encountered in the Osamu Utsumi mine was the main objective, the secondary objective being to do the same for the nepheline phonolite found in the region. Figure 2 shows the locations of the various samples that were taken for subsequent analysis. Tables II and III show the Rb-Sr and Sm-Nd elemental and isotope values used for these geochronological studies.

MSWD (mean square of the weighted deviations) is an expression of how well the isochron fits the data. Based upon the very high precision attained (blanket 1σ errors conservatively estimated at ± 0.5% in ^{87}Rb/^{86}Sr and ±0.0017% in ^{87}Sr/^{86}Sr), an MSWD value less than 2 is considered to indicate that the fitted line falls within analytical error and therefore represents a true isochron. Values of MSWD much greater than 2 would suggest that the data fall off of the fitted line possibly due to "geological" error (e.g. sample inhomogeneity, non-closed system, non-consanguinity of samples) and would therefore be designated as an "errorchron". Ages based upon errorchrons are equivocal at best, particularly if the Rb/Sr ratio is low.

Figure 4 shows all regional samples plotted on a ^{87}Sr/^{86}Sr versus ^{87}Rb/^{86}Sr diagram. The regression analysis of the four nepheline syenite bulk samples and a model initial ^{87}Sr/^{86}Sr value of 0.70511 yields an age of 74.2(6.3) Ma with an MSWD = 2.72. The model initial ^{87}Sr/^{86}Sr value of 0.70511 is based upon the strong tendency of numerous regressions of appropriately selected rock sample groups towards such an initial value. The results of this particular regression are considered to exhibit noticeable geological error (MSWD > 2) and therefore represent an errorchron. This failure of isochron conditions is mainly due to a small number (4) of data points, and the very small range in ^{87}Rb/^{86}Sr (0.13 to 0.23).

TABLE II

Rb-Sr analytical data for Poços de Caldas regional samples.

Sample	Rb (ppm)	Sr (ppm)	^{87}Rb/^{86}Sr	^{87}Sr/^{86}Sr^{a}	^{87}Sr/^{86}Sr$_{\text{initial}}$^{b}
PH-2A	194.6	2208.	0.2549	0.705644 (6) 0.705652 (7)	0.705362 (16)
PH-2B	183.4	2146.	0.2472	0.705627 (8)	0.705353 (16)
PH-3	174.1	1388.	0.3628	0.705500 (10)	0.705104 (20)
PH-5	167.3	1385.	0.3492	0.705483 (7) 0.705492 (15)	0.705096 (19)
PH-8	181.1	1705.	0.3074	0.705532 (9)	0.705191 (17)
PH-9B	183.5	1769.	0.3001	0.705500 (8)	0.705167 (17)
NS-1	170.0	2130.	0.2309	0.705335 (7)	0.705079 (15)
NS-4	162.0	2902.	0.1614	0.705274 (8)	0.705095 (12)
NS-6	148.8	3263.	0.1319	0.705250 (7)	0.705104 (12)
NS-7	159.5	2865.	0.1610	0.705309 (8)	0.705131 (12)
NS-7 mineral separates					
sphene ?#1	8.877	5038	0.00510	0.705121 (11)	0.705115
sphene ?#2	14.13	6242	0.00655	0.705133 (10)	0.705126
aegirine	0.648	291.2	0.00644	0.705105 (12)	0.705102
K-feldspar	229.4	2605	0.2547	0.705398 (8)	0.705116
nepheline	12.89	186.5	0.2000	0.705326 (12) 0.705332 (14)	0.705104

[a] Measured values normalized assuming normal Sr with ^{86}Sr/^{88}Sr = 0.119400. Uncertainties refer to the last digit(s) and are two standard deviations of the mean for in-run statistics. Duplicate entries are repeat mass spectrometer runs.

[b] Calculated ratio for 78 Ma ago with one-sigma uncertainties in last digits which take into account uncertainties in age (±3 Ma), measured ^{87}Rb/^{86}Sr (±0.5%) and measured ^{87}Sr/^{86}Sr using a ^{87}Rb decay constant of 1.42×10^{-11} a^{-1}.

Figure 5 is an internal isochron fitted for the mineral separates of NS-7, as well as that of bulk NS-7 (n=6). The initial ^{87}Sr/^{86}Sr ratio for this grouping of samples is 0.70512(1). The age associated with this isochron is 77.9(3.1) Ma, and the MSWD is 0.88. The variables associated with the above isochrons are based upon the regression algorithm of McIntyre Model I (Brooks *et al.*, 1972).

A regression calculation was also made for the NS-7 mineral separates alone (n=5), without including bulk NS-7, since for some unknown reason this datum lies the furthest away from the isochron. Again, using the McIntyre Model I regression program,

TABLE III

Sm-Nd analytical data for Poços de Caldas regional samples.

Sample	Sm (ppm)	Nd (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$[a]	$^{143}Nd/^{144}Nd$ initial[b]
PH-2A	9.335	82.40	0.06848	0.512347 (4)	0.512308 (6)
PH-2B	9.316	82.03	0.06865	0.512341 (5)	0.512302 (6)
PH-3	15.80	124.3	0.07683	0.512402 (4)	0.512359 (6)
PH-5	15.90	125.7	0.07647	0.512412 (5)	0.512369 (6)
PH-8	14.63	110.8	0.07981	0.512393 (5)	0.512348 (6)
PH-9B	15.21	125.4	0.07334	0.512376 (7)	0.512335 (6)
NS-1	16.11	122.6	0.07942	0.512404 (5)	0.512359 (6)
NS-4	19.01	139.9	0.08212	0.512403 (8)	0.512357 (7)
NS-6	19.40	140.9	0.08323	0.512407 (5)	0.512360 (6)
NS-7	10.19	78.19	0.07879	0.512405 (5)	0.512361 (6)

[a] Measured values normalized assuming normal Nd with $^{146}Nd/^{144}Nd = 0.721900$. Uncertainties in the last digit(s), given in parentheses, are two standard deviations of the mean for in-run statistics.

[b] Calculated ratio for 78 Ma ago with one-sigma uncertainties in last digits which take into account uncertainties in age (±3 Ma), measured $^{147}Sm/^{144}Nd$ (±0.1%) and measured $^{143}Nd/^{144}Nd$ using a ^{147}Sm decay constant of 6.54×10^{-12} a^{-1}.

$(^{87}Sr/^{86}Sr)_i$ equals 0.70511(1), age equals 77.4(3.4) Ma, and MSWD equals 0.73. The differences between these regression values and those including NS-7 are not very significant.

It should be noted that the $^{87}Rb/^{86}Sr$ values for all the regional bulk samples analyzed are very low with a relatively small overall range (0.13 to 0.35), such that the very high precision measurement of $^{87}Rb/^{86}Sr$ is almost essential in order to determine meaningful isochron parameters. The $^{87}Rb/^{86}Sr$ values for the mineral separates of NS-7 are also quite low (0.002 to 0.26). These low $^{87}Rb/^{86}SR$ values are apparently typical of nepheline syenites (e.g. Lameyre and Lasserre, 1967; Vitrac-Michard *et al.*, 1977; Liegeois *et al.*, 1983).

Therefore, based upon numerous regressions of other groupings of the regional nepheline syenite and phonolite samples, as well as the above NS-7 internal isochron, the following model values are considered to be representative of unaltered nepheline syenite of the Poços de Caldas plateau: the $(^{87}Sr/^{86}Sr)_i$ value is taken to be 0.70511(1), and the age is estimated to be 78(3) Ma.

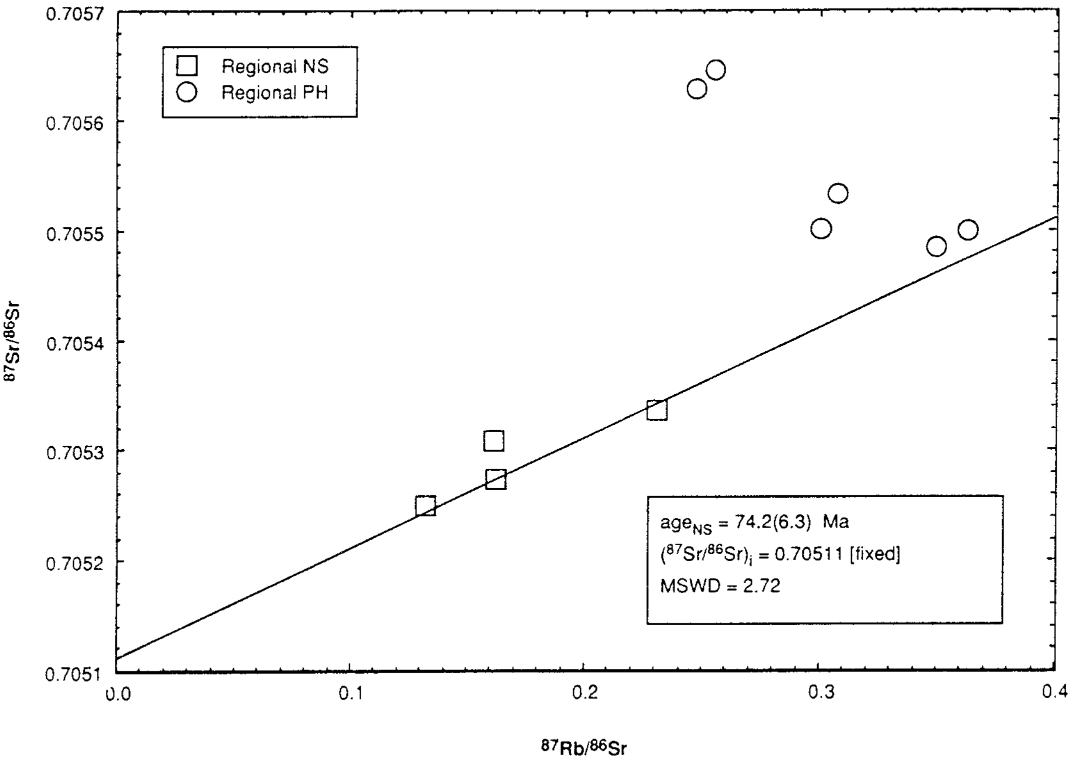

Figure 4. Whole-rock Rb-Sr errorchron for Poços de Caldas regional nepheline syenites (open squares). The derived age is 74.2(6.3) Ma, using a model initial $^{87}Sr/^{86}Sr$ ratio of 0.70511. The MSWD for the fitting of these nepheline syenites is 2.72, indicating likely geological error. Regional phonolites (open circles) are also plotted and do not fall on this fitted line, revealing apparently distinct volcanic piles.

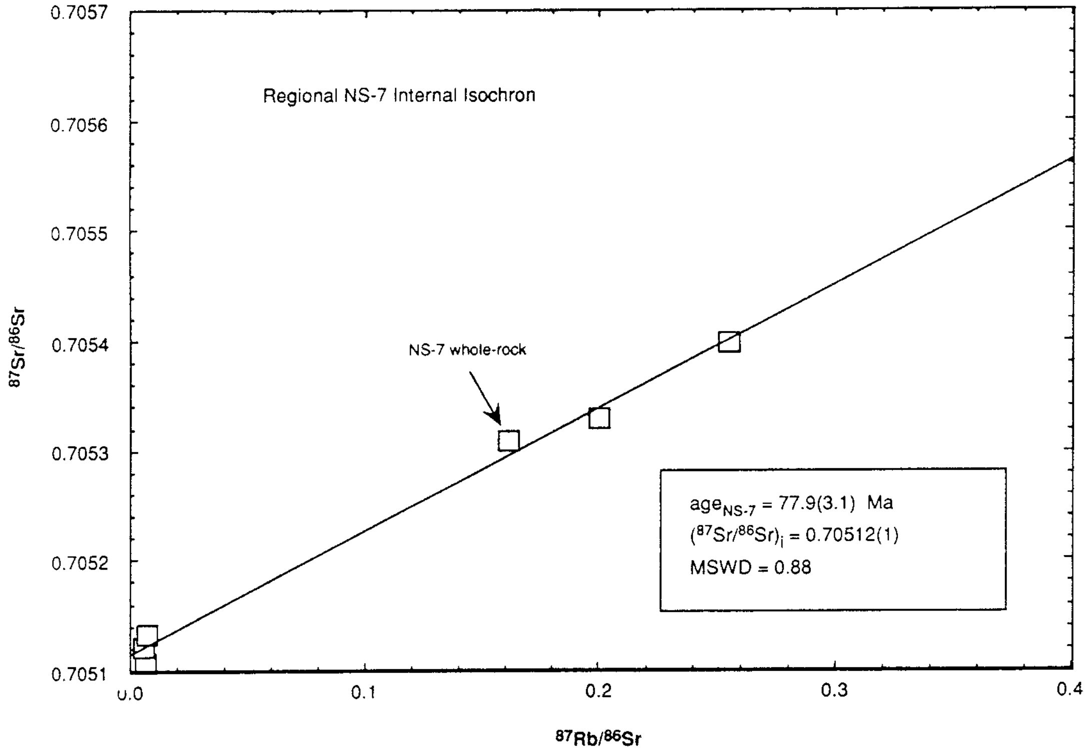

Figure 5. Internal Rb-Sr isochron from mineral separates of nepheline syenite sample NS-7. The derived age is 77.9(3.1) Ma, with an initial ^{87}Sr/^{86}Sr ratio of 0.70512(1). The MSWD for the fitted line is 0.88. The bulk NS-7 value lies just off the isochron. This isochron age was used to give the model nepheline syenite age of 78(3) Ma.

It is not known unequivocally whether the central nepheline syenite body is the same as, or representative of, the nepheline syenite found in the Osamu Utsumi mine. There are possibly two other bodies, as mapped by Ulbrich (1985), which may represent the mine nepheline syenite. However, there is little reason, and no previously reported data, to believe that these bodies would differ significantly in either age or initial (unaltered) stable and radiogenic isotopic signature. Given the fact that these data come very close to falling on the nepheline syenite isochron, it is very possible that the nepheline phonolite west of the central nepheline syenite body is consanguineous to that body, having the same initial $^{87}Sr/^{86}Sr$ value, and slightly older than that body.

The other regional nepheline phonolite samples, collected from areas designated as phonolite by Ulbrich (1985), do not fall near the NS-7 isochron (see Fig. 4). Samples PH-2A and PH-2B are from a quarry within nepheline phonolite that lies between the fluorite-bearing nepheline syenite body that Kawashita *et al.* (1984) studied and the olivine nephelinite of Amaral *et al.* (1967) and Bushee (1971). Samples PH-8 and PH-9B are from a relatively large exposure of nepheline phonolite in the southern portion of the caldera. From the limited data obtained on these nepheline phonolite samples, it appears that these "groups" represent volcanic piles that are distinct from the one previously noted to possibly be related to the central nepheline syenite body. In order to determine the age relations of these two "groups", further sampling and analysis would be required.

Based upon the above considerations, it is apparent that the bulk NS and PH samples, either collectively or as groups, do not provide significant chronological information. This is due to the rocks being of different age and/or having different initial $^{87}Sr/^{86}Sr$ values, or to post-crystallization disturbance.

3.4. Petrogenesis

Figure 6 shows the $(^{87}Sr/^{86}Sr)_i$ value for the regional nepheline syenite and phonolite as a function of their $\delta^{18}O$ value. The nepheline syenite shows a roughly horizontal trend. Considering the papers of Fleck and Criss (1985), Criss and Fleck (1986) and Taylor (1986), these data can be interpreted as follows. The relatively moderate $(^{87}Sr/^{86}Sr)_i$ values, as previously noted, are possibly indicative of a mantle source for the alkaline magmatism, with some incorporation of old or high Rb/Sr material, which typifies crustal material. The relatively high (greater-than-mantle) values of $\delta^{18}O$, if not due to surficial processes, would also seem to require some assimilation of crustal, mantle

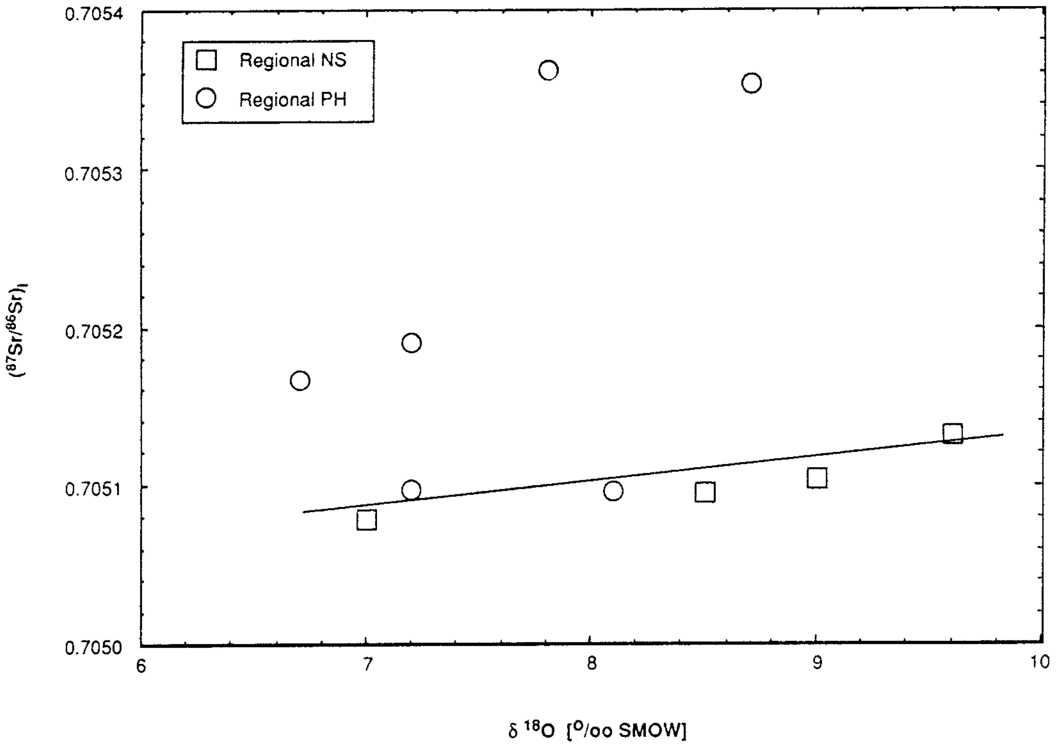

Figure 6. The ($^{87}Sr/^{86}Sr)_i$ value for the regional nepheline syenite and phonolite as a function of their $\delta^{18}O$ value. The low $^{87}Sr/^{86}Sr$ values of the nepheline syenite (dashed line) are likely indicative of a primitive source, whereas the greater-than-mantle $\delta^{18}O$ values indicate either crustal assimilation, mantle metasomatism, or recycling of previously $\delta^{18}O$ enriched (e.g. oceanic crust) material. The nepheline phonolite values probably exhibit later incorporation of radiogenic ^{87}Sr.

metasomatized (source?) or recycled and previously $\delta^{18}O$ enriched (oceanic crust?) material. The regional phonolite samples exhibit a distinct separation from this trend.

The Sm-Nd data presented in Table III are shown graphically in Figure 7. Although the nepheline syenite data lie on the calculated model isochron, they do not define the isochron, which is probably due to two major factors.

First, the rocks of Poços de Caldas are quite young to be dated in any meaningful way using Sm-Nd systematics, where $\lambda(^{147}Sm) = 6.54x10^{-12}$ [a^{-1}] and $t_{1/2} = 1.06x10^{11}$ [a]. Thus, there has been insufficient time for the Sm-Nd systematics to develop an isochron containing any significant temporal information.

Second, since the analytical precision obtained is sufficiently high, it appears that what we are seeing is the initial heterogeneity of $^{143}Nd/^{144}Nd$ within the nepheline syenites.

The regional phonolite samples clearly lie off of the model isochron. This open system behavior is probably due to the phonolite samples having different initial $^{143}Nd/^{144}Nd$ values.

Therefore, the results of the Sm-Nd data are best applied in a petrogenetic sense. Figure 8 shows initial $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ data, plotted as $\epsilon_{Sr}(T)$ and $\epsilon_{Nd}(T)$ using the notation and formulation of DePaolo (1988). The $(^{87}Sr/^{86}Sr)_i$ values of 0.70510 to 0.70536 (average = 0.70521 ± 0.00012, n=6) for the nepheline phonolites fall within the majority and very close to the average value (0.70577, n=417) for continental volcanic rocks. The $(^{143}Nd/^{144}Nd)_i$ values of 0.512306 to 0.512373 (average = 0.512341 ± 0.000028, n=6) also fall within the majority, but further away from the average value (Faure, 1986).

The Poços de Caldas nepheline phonolite and syenite data lie within the "Mantle Array" trend, as defined by ocean island basalts (OIB). For the sake of convenience, and as a reference guide, we plot the Mantle Array as $\epsilon_{Nd} = 0.4\ \epsilon_{Sr} \pm 2$. The majority of the Poços de Caldas nepheline phonolite data cluster around a value of $\epsilon_{Sr}(T) = +11 \pm 2$ and $\epsilon_{Nd}(T) = -4 \pm 0.5$. The nepheline syenite data (n=4) define a much tighter cluster with coordinates of $\epsilon_{Sr}(T) = +9.8 \pm 0.3$ and $\epsilon_{Nd}(T) = -3.4 \pm 0.0$, which lies within the nepheline phonolite field.

These data fall just within quadrant IV of an ϵ_{Nd} vs ϵ_{Sr} diagram, in which almost all continental volcanic provinces have representatives (Faure, 1986). There are two main hypotheses that could explain the presence of rocks, and by inference the Poços de Caldas data, within this quadrant: Model 1) the alkaline rocks in question could have been derived from a source enriched in Rb (hence positive ϵ_{Sr} values) and depleted in Sm (hence negative ϵ_{Nd} values) relative to primitive mantle, and remained isolated for a sufficient period of time in order to develop and retain that distinct isotopic signature; Model 2) the source magma of the alkaline rocks could have been contaminated with

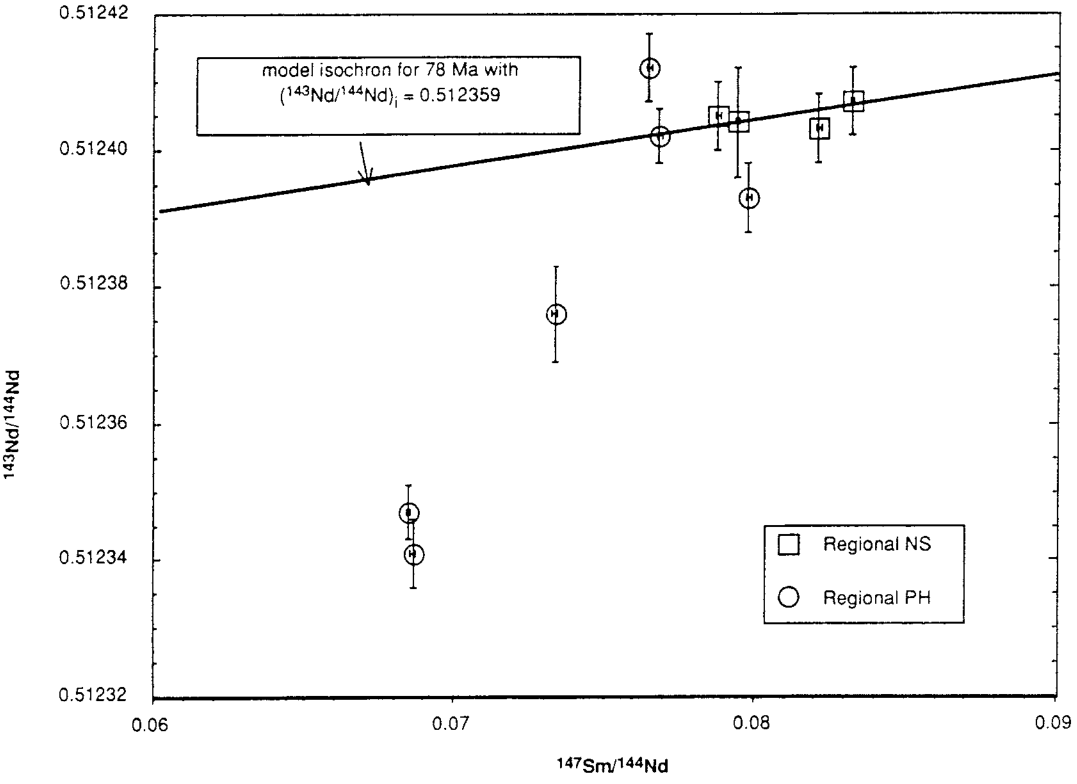

Figure 7. Sm-Nd data for Poços de Caldas regional nepheline syenite (open squares) and phonolite (open circles) with error bars indicated. The lack of a defined isochron is likely due to the rocks being too young for Sm-Nd dating. Thus these data exhibit the initial heterogeneity of the Sm-Nd system within the rocks. The nepheline syenite samples conform very well to a model isochron, whereas the phonolites exhibit marked open system behavior.

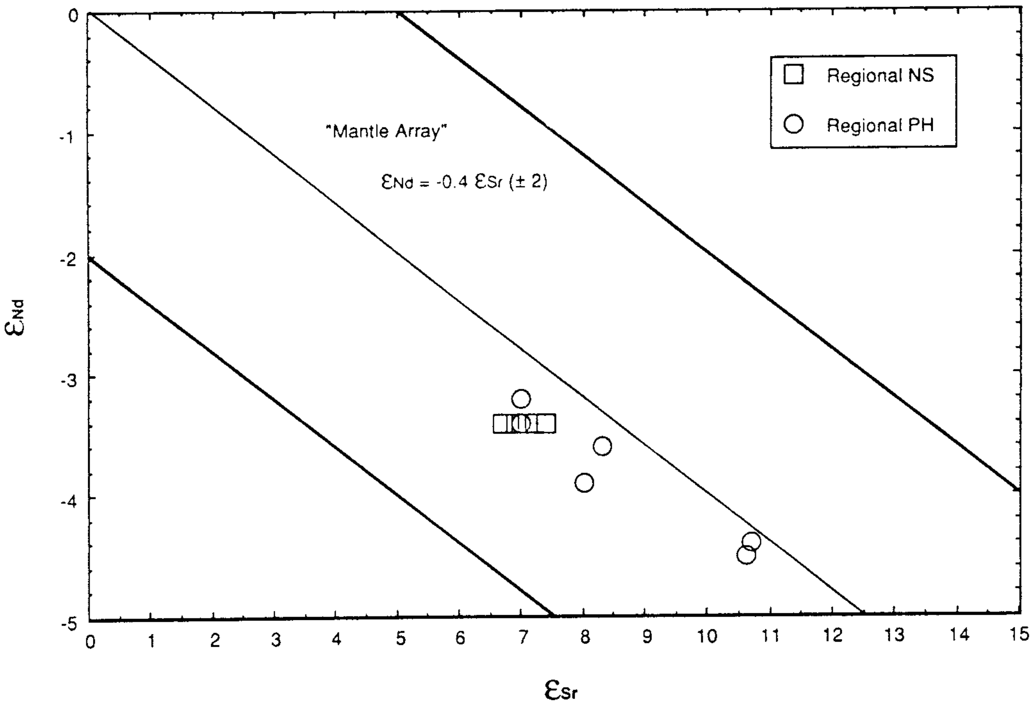

Figure 8. Initial $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ data for the Poços de Caldas regional nepheline syenite (open squares) and phonolite (open circles) expressed as $\epsilon_{Sr}(T)$ and $\epsilon_{Nd}(T)$. The data lie within the Mantle Array trend and likely indicate that the primitive source magma was contaminated by continental metamorphic rocks.

Nd and Sr derived from continental igneous and metamorphic rocks which are typically enriched in Rb and depleted in Sm. The source magma in this second scenario would likely be from somewhere towards or within quadrant II (negative ϵ_{Sr} and positive ϵ_{Nd} values), representing sources similar to an asthenospheric Mid Ocean Ridge Basalt (MORB)-type mantle.

Mantle metasomatism (Lloyd and Bailey, 1975; Bailey, 1987) is one possible model that explains the generation of alkaline melts, based mainly on the evidence that mantle-derived inclusions within alkaline rocks have experienced varying degrees of metasomatism.

According to the mantle metasomatism model, sterile, refractory, Mg-rich peridotite which has been variably depleted by previous extraction of basaltic partial melts is: (1) infiltrated by solutions that modify its bulk chemical and mineralogical composition, and (2) this metasomatically altered mantle material is partially melted, triggered by the increase in volatile content, giving rise to alkaline magma. The metasomatizing fluid composition is likely high in H_2O, may be high in CO_2, contains variably high concentrations of such incompatible and Large Ion Lithophile (LIL) elements as H, C, F, Na, Al, P, S, Cl, K, Ca, Ti, Fe, Rb, Y, Zr, Nb, Ba and REE, and could be either aqueous fluids at submagmatic temperatures or volatile rich silicate melts (Best, 1982).

However, it now appears that most petrologists believe that alkaline magma is produced by the fractional crystallization of basic magma and there is recognition of mantle metasomatism and its possible role as a precursor to alkaline magmatism. Furthermore, mantle metasomatism itself may be caused by alkaline magmatism (Fitton and Upton, 1987).

Mantle metasomatic alkaline magmatism requires that the mantle source lie within regions of the lithosphere, typically referred to as the continental lithospheric mantle, where metasomatically enriched material can remain isolated from convection, akin to model (1) above. However, Menzies (1987) has noted, based upon Rb-Sr and Sm-Nd isotopes, that the majority of inclusion-bearing alkaline rocks have a source region identical with that of OIB, regardless of whether they are erupted through oceanic or continental crust. He concludes that their source is not within the lithosphere, but in or below the convecting asthenosphere. Fitton (1987) studied the Cameroon line, an intra-plate alkaline volcanic province which crosscuts a continental margin, and found no significant chemical or isotopic (Rb-Sr) differences between the oceanic and continental sectors. Foland *et al.* (1988) have studied the Mesozoic plutonic complexes of north-eastern North America (e.g. White Mountain series province) and the New England Seamounts which form a line, in a similar sense to the Cameroon line, that traverses from continent to ocean. They found that the isotopic signatures of the parental alkaline to subalkaline magmas, broadly similar to OIB, were similar for the continental plutons and the seamounts, although crustal contamination had to be taken into account. These observations would support Model (2) above.

With regard to the Poços de Caldas volcanics, it would seem more likely that the second mechanism above was responsible for the observed ϵ_{Sr} and ϵ_{Nd} values. This would be true mainly because of the presence of Precambrian schist surrounding the Poços de Caldas plateau (the source of continental Sr and Nd contamination), and the apparent primitive nature of the source magma, as implied by the presence of the volcanic $\epsilon_{Sr}(T)$ and $\epsilon_{Nd}(T)$ values within the terminus of the Mantle Array trend.

4. Drillcore F4 studies, Osamu Utsumi mine

A cored borehole F4 (8-1UK11) was drilled in the mine in order to: (1) sample a profile through one of the main hydrothermally altered and mineralized breccia bodies found at the mine; (2) sample the primary hydrothermal mineralization and associated host rocks at depth; and (3) sample the nepheline syenite that hosts the mineralized breccia body.

The first objective was fairly successful, with five nepheline syenite samples and three nepheline phonolite samples being selected and analyzed in the top approximately 265 m of the core. These samples are referred to as the F4-NS (22, 39, 91, 107, 265) and F4-PH (19, 123, and 129) series, respectively. The sample numbers are approximately equal to the core length at which they were sampled. These samples lie within the oxidized, reduced and mineralized zones as generally recognized within the mine.

The second objective was not as successful. An analysis was made of geochemical survey boreholes used for guiding mining operations in order to direct the orientation of the F4 core through a perceived elevated mineralized "pod". The determined true angle of dip, in the direction of S 18°W, was 55° to the south. Figure 9 shows a simplified geological cross-section in which the F4 core lies. It was hoped that the drillcore would intercept a mineralized vein, crosscutting either nepheline syenite, phonolite, or both within the breccia body. Although some mineralization was seen, no clear crosscutting relationships were observed upon which I could confidently base meaningful sampling, analysis, and interpretation.

The third objective was moderately successful. It was expected that the drillcore would intercept the contact between the nepheline syenite host rock and the breccia body at a

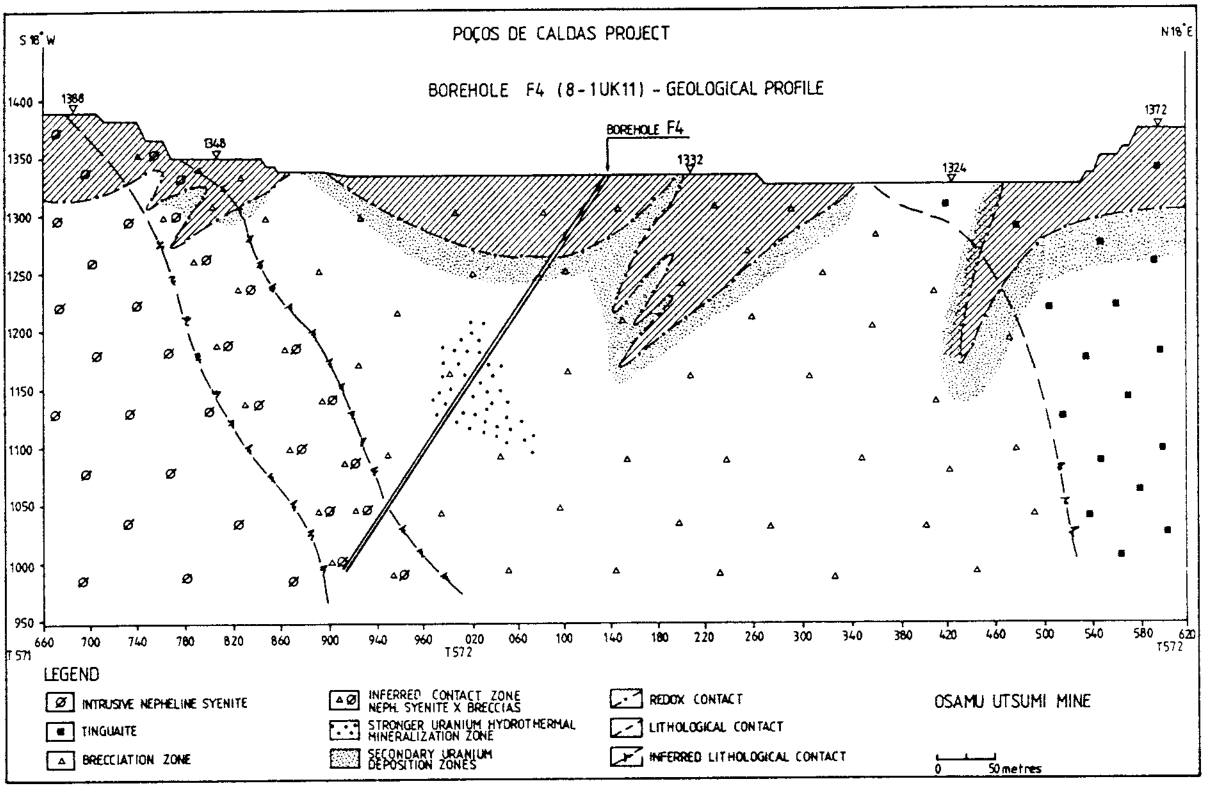

Figure 9. A simplified and schematic geological cross-section of the portion of the Osamu Utsumi mine where the F4 drillcore lies. The borehole is shown to pass through the breccia body, intersecting at an angle oxidized rocks, secondary uranium enrichment, hydrothermal uranium "pod", and ending within a transition "zone" towards the host nepheline syenite.

core length of approximately 275 m, and at an approximate depth of 1100 m above sea level. However, instead of finding continuous nepheline syenite beyond a distinct nepheline syenite/breccia boundary, I found that the brecciation attenuated. This was expressed by the spacing of phonolitic dykes separating nepheline syenite "blocks" becoming greater with depth. Drilling was finally stopped at a core length of approximately 415 m, and unknown depth. An especially continuous length of nepheline syenite found between approximately 412 and 413 m was sampled and analyzed as representative of the nepheline syenite host rock proximal to the breccia body. This length of core (sometimes referred to as a "xenolith") was sampled approximately equidimensionally both as five relatively large "average" samples and as 16 approximately 1 cm-wide "finer scale" samples. These samples are referred to as F4-413-NS-Average (AA to AE) and F4-413-NS-Series (A to P).

Instead of finding a highly mineralized sample to fulfill the second criteria above, another sample was selected and analyzed. This sample contains three lithologies: nepheline that has apparently experienced hydrothermal alteration (F4-353-NS1), a phonolitic dyke (F4-353-VD) and a strongly brecciated nepheline syenite, comprising nepheline syenite plus phonolite fragments within a fine-grained clay matrix (F4-353-NS2). This sample is discussed in more detail in Waber *et al.* (this report series; Rep. 2).

A lamproite dyke was also sampled, as exposed within the Osamu Utsumi mine, which appears to crosscut the hydrothermal alteration at the mine. This dyke was sampled in order to help bracket the age of the hydrothermal alteration, and therefore the age of primary mineralization (as opposed to secondary supergene enrichment). This lamproite dyke is discussed further in section 5.

4.1. Geology and petrology

The geology and elemental geochemistry of the Osamu Utsumi mine are discussed in more detail in Waber *et al.* (op. cit.) and Schorscher and Shea (this report series; Rep. 1). The following is a brief summary based upon these reports.

The Osamu Utsumi mine is located approximately 15 km south of the city of Poços de Caldas. The mine area exhibits primary uranium mineralization disseminated in hydrothermally altered rocks, high-grade Zr-REE vein-type mineralization and supergene uranium enrichment associated with iron redox fronts.

The rocks found within the mine area comprise hydrothermally and metasomatically altered nepheline syenites and volcanic to subvolcanic nepheline phonolites. Crosscutting these rocks are two major breccia pipes. Late stage lamproite dykes crosscut all of the rocks and breccia and do not appear to be hydrothermally altered. Superimposed on the high-temperature alteration is a supergene redox-controlled deep weathering which has caused a secondary enrichment of uranium.

The Osamu Utsumi mine has been subdivided into three main mining areas, namely ore-bodies A, B and E. These areas differ geologically and exhibit different mineralization characteristics.

The F4 drillcore, which is the focus of this study, is sampled through ore-body B which has a complex lithology and is composed of nepheline syenites ("foyaites"), leucocratic phonolites, clinopyroxene-bearing phonolites and pseudo-leucite phonolites. There is intense brecciation of the country rock. Primary mineralization is both disseminated and vein type in nature; the latter is typically an infilling between breccia blocks.

The nepheline syenite intrusives found at the Osamu Utsumi mine, which act as country rock for much of the breccia pipes, are most likely the same as the regional nepheline syenite. These nepheline syenites have intruded into older nepheline phonolites, with both subsequently being fractured and further intruded by younger phonolitic "dykes" and related volatiles and volcanic phases.

4.2. Water/rock interaction

As previously noted, the rocks of the Osamu Utsumi mine have experienced variable degrees of hydrothermal mineralization and metasomatism, and deep weathering. These are all found within the F4 drillcore. Of particular interest to this study is the hydrothermal alteration. Important aspects of this alteration, which are discussed in detail in other related papers, include thermal, chemical and hydrologic modeling (Cathles and Shea, this report series; Rep. 13) and mineralogical and elemental chemical studies (Schorscher and Shea and Waber *et al.*, this report series; Reps. 1 and 2).

Table IV contains the δD and $\delta^{18}O$ values for the F4-NS, F4-PH and F4-413 sample groups. These values are displayed in Figure 10, along with the regional nepheline syenites and phonolites that were previously discussed and displayed in Figure 3 in section 3.2.

A general observation from these values, particularly relative to the regional data, is that they exhibit a trend away from the regional values along a marked δD interaction

TABLE IV

Stable isotopes (δD and $\delta^{18}O$) for nepheline syenite samples from the Osamu Utsumi mine F4 borehole.

Sample	δD SMOW[$^{o}/_{oo}$][1]	$\delta^{18}O$ SMOW[$^{o}/_{oo}$][2]
F4 Nepheline syenites		
F4-39-1A	-62/-66**	+6.5
F4-91-1B	-46	+6.2**
F4-107-1A	-46	+9.0
F4-265-1A	-45	+9.1
F4 413 Nepheline syenite xenolith series		
F4-413-1A-A	-77	+7.1
F4-413-1A-B	-72	+6.4
F4-413-1A-C	-66	+7.2
F4-413-1A-D	-82	+6.9
F4-413-1A-E	-72	+7.0
F4-413-1A-F	-79	+6.2/+6.5**
F4-413-1A-G	-69	+6.6
F4-413-1A-H	-58	+5.7
F4-413-1A-I	-51	+5.7
F4-413-1A-K	-54	+6.9/+6.8**
F4-413-1A-L	-58	+6.1
F4-413-1A-M	-70	+5.9
F4-413-1A-N	-61	+6.2
F4-413-1A-O	-63	+6.0
F4-413-1A-P	-75	+5.6
F4-413-1AA	-47	+5.9
F4-413-1AC	-50	+6.3
F4-413-1AE	-67	+7.4

[1] 2σ uncertainties for δD are ± 2 [$^{o}/_{oo}$].

[2] 2σ uncertainties for $\delta^{18}O$ are ± 0.4 [$^{o}/_{oo}$].

**Average of duplicate analyses on separate aliquots of sample.

track. As previously discussed, a possible isotopic value for this meteoric water would be approximately $\delta D = -50 \pm 5$ and $\delta^{18}O = -7.5 \pm 0.5$.

The δD shift of these hydrothermally altered rocks, with only a very slight $\delta^{18}O$ shift, is quite pronounced. This lack of significant $\delta^{18}O$ shift could be interpreted as indicative of a relative immaturity of the water/rock exchange within the breccia pipe (Blattner, 1985), assuming that the interacting hydrothermal water was meteoric in origin. However, as discussed further in Cathles and Shea (this report series; Rep. 13), the breccia pipe has experienced marked water/rock interaction.

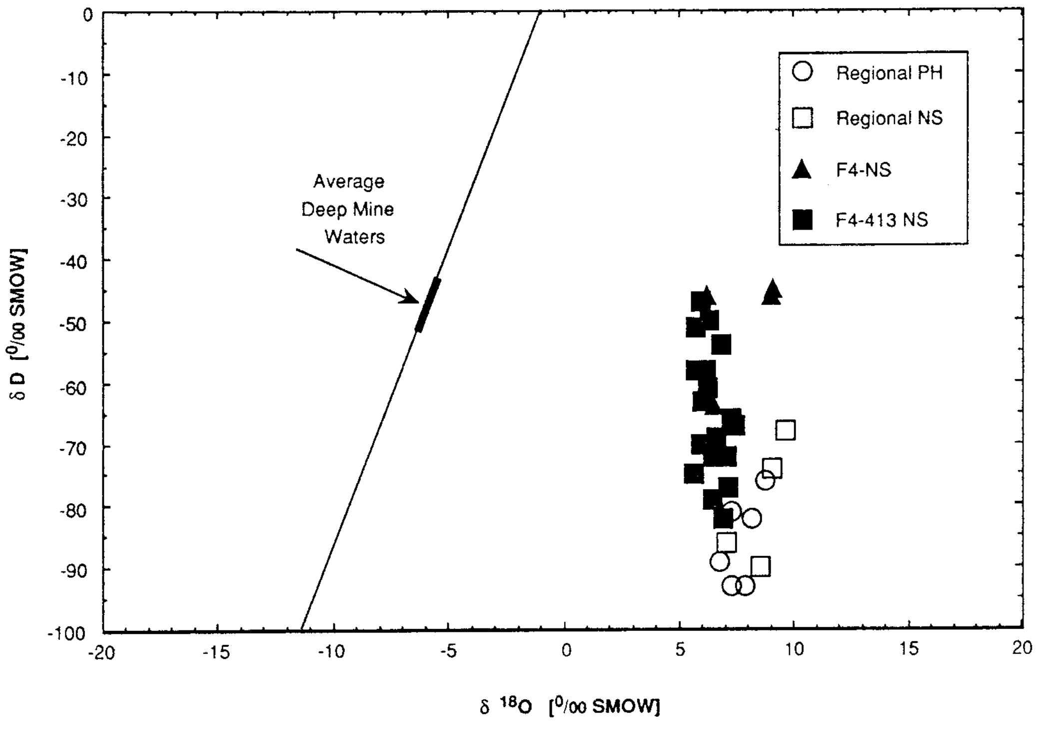

Figure 10. δD and $\delta^{18}O$ values for Poços de Caldas regional nepheline syenite (open squares), and phonolite (open circles), F4 nepheline syenites (closed triangles) and F4-413 nepheline syenites (closed squares). The F4 samples show a marked δD shift up towards the average deep mine water values, with very little $\delta^{18}O$ shift. The δD and $\delta^{18}O$ distribution possibly reflect the position of the F4 drillcore and breccia body within the palaeohydrothermal regime.

Another possibility which comes to mind is that the interacting hydrothermal fluids are not of mainly meteoric origin, but are possibly "magmatic", having previously isotopically equilibrated with the rock. This could explain the absence of an oxygen isotopic shift, but makes it difficult to explain how the hydrogen isotopic shift takes place, and places unrealistic constraints on the amount of fluid which is available for interaction.

The location of samples along the drillcore through the breccia body, and indirectly within the palaeohydrothermal regime, might also account for the lack of apparent $\delta^{18}O$ shift. One possibility is sampling bias, where one "misses" the $\delta^{18}O$ shifted rock, either because the drillcore did not pass through this exchanged rock or it was not sampled along the core. A second possibility is that the spatial distribution of $\delta^{18}O$ exchange associated with the breccia body within the palaeohydrothermal regime, especially as integrated through time, is distinctly heterogeneous.

I do not believe that the lack of $\delta^{18}O$ shift is the result of sampling bias. The samples analyzed and shown in Figure 10 are for nepheline syenites near the bottom of the drillcore (F4-413 series) and nepheline syenites from the middle all the way to the near-surface (F4-265, F4-107, F4-91, F4-39, and F4-22), where the sample numbers roughly represent the length along the drillcore where they were sampled from. The relatively high $\delta^{18}O$ values for samples F4-107-1A and F4-265-1A are due to the samples coming from the highly mineralized zone of the breccia body. Thus, it is not surprising that the δD and $\delta^{18}O$ values for the F4-413 series, which are presumably at least approaching "fresh rock" status towards the end of the drillcore, as well as the nepheline syenite host rock for the breccia pipe, more or less overlap with the δD and $\delta^{18}O$ values of the presumably most altered of the regional nepheline syenites.

The absence of homogeneity of the δD values most likely reflects the variability of temperature, hydrologic flow and, therefore, water/rock interaction and isotopic exchange in the palaeohydrothermal regime. It is likely that the length of the F4 drillcore lies within a portion of the palaeohydrothermal regime which vertically homogenized the $\delta^{18}O$ signature of the rock, with only a slight $\delta^{18}O$ shift. The δD trend is probably due to the sampled rocks being variably altered and reflects gradation of time-integrated water/rock interaction.

The aspects of this temporal and geometrical variability of the Poços de Caldas breccia palaeohydrothermal regime have been modelled and are discussed in Cathles and Shea (this report series; Rep. 13).

4.3. Geochronology

Tables V and VI show the Rb-Sr and Sm-Nd isotopic data for the F4-NS plus F4-PH and F4-413 sample series. The Rb-Sr isochron is plotted for the F4-413 group in Figure 11.

The regression of the F4-413 sample series has considerable geochronological importance to this study. The McIntyre model I regression through all of the F4-413 samples yielded an age of 75.8(1.2) Ma and an initial $^{87}Sr/^{86}Sr$ value of 0.70532 ± 0.00011, with a MSWD of 1.08. Another regression was performed by removing sample F4-413-AE, which was an outlier by just over 2 sigma, from the regression. This new McIntyre model I regression yielded an age of 76.0(1.2) Ma and an initial $^{87}Sr/^{86}Sr$ value of 0.70529 ± 0.00011, with a MSWD of 0.58. Since the results of these two regressions are the same within the analytical uncertainty, the results of F4-413 including subsample AE are shown in Figure 11.

As discussed in Waber *et al.* and Cathles and Shea (this report series; Reps. 2 and 13), the elemental distribution exhibited for the F4-413 series samples shows clear evidence of hydrothermal alteration. The F4 mine samples demonstrate significant enrichment in Rb, as well as K, relative to their proposed regional precursors. Thus the increase in the initial $^{87}Sr/^{86}Sr$ values may in part be an incorporation of radiogenic ^{87}Sr produced by approximately 2 Ma of ^{87}Rb decay. There may also have been an incorporation of radiogenic ^{87}Sr from a volume of rock significantly larger than the F4-413 rock itself. The F4-413 samples also exhibit an increase in their Rb/Sr ratio, as well as an approximate fifty-fold increase in their $^{87}Rb/^{86}Sr$ (approximately 5.0 to 7.5) ratios relative to regional nepheline syenites (approximately 0.15 to 0.25). It is also possible that these changes were brought about by Sr removal, as well as Rb enrichment.

I interpret the above as evidence that the hydrothermal water/rock interaction has apparently isotopically re-equilibrated the Rb-Sr systematics of this large nepheline syenite xenolithic sample. Thus the age of the F4-413 sample series is the same as that of the hydrothermal event that caused the isotopic homogenization. In turn, this is the age of primary mineralization as found in the mine. Therefore, based upon the Rb-Sr systematics of F4-413, my model age for the hydrothermal, primary mineralization event(s) is 76(2) Ma.

A study of $(^{87}Sr/^{86}Sr)_i$ values relative to 1/Sr elemental concentration is often a useful indication of mixing within the Rb-Sr system. Figure 12 shows such a mixing diagram for Poços de Caldas regional and F4 nepheline syenite and phonolite samples.

TABLE V

Rb-Sr analytical data for Poços de Caldas F4 samples.

Sample	Rb (ppm)	Sr (ppm)	$^{87}\mathrm{Rb}/^{86}\mathrm{Sr}$	$^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$[a]	$^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ initial[b]
F4 Nepheline syenites					
F4-39-1A	305.9	106.7	8.301	0.714335 (15)	0.70514 (13)
F4-39-1A	303.6	106.1	8.287	0.714294 (12)	0.70511 (13)
F4-91-1B	344.7	382.3	2.609	0.707936 (8)	0.70504 (4)
F4-107-1A	254.1	413.8	1.777	0.707061 (9)	0.70509 (3)
F4-265-1A	294.9	357.2	2.388	0.707510 (9)	0.70486 (4)
F4-265-1A	293.6	387.9	2.190	0.707437 (10)	0.70501 (4)
Osamu Utsumi lamproite dyke					
Biotite	638.1	516.7	3.573	0.706699 (6)	
F4 413 Nepheline syenite xenolith					
F4-413-1A-A	418.3	174.9	6.924	0.712807 (9)	0.70513 (11)
F4-413-1A-A	419.1	171.6	7.071	0.712898 (8)	0.70506 (11)
F4-413-1A-C	419.6	172.7	7.034	0.712889 (9)	0.70509 (11)
F4-413-1A-E	434.3	184.7	6.807	0.712635 (14)	0.70509 (10)
F4-413-1A-H	420.0	168.4	7.222	0.713119 (15)	0.70512 (11)
F4-413-1A-L	435.7	240.6	5.241	0.710941 (11)	0.70513 (8)
F4-413-1A-N	439.6	194.5	6.543	0.712308 (7)	0.70506 (10)
F4-413-1A-P	422.4	204.4	5.983	0.711740 (9)	0.70511 (9)
F4-413-1AA	426.3	205.2	6.013	0.711768 (12)	0.70510 (9)
F4-413-1AC	432.9	229.3	5.464	0.711229 (11)	0.70517 (8)
F4-413-1AE	423.1	203.2	6.027	0.711900 (8)	0.70522 (9)
				0.711890 (11)	
F4-413-1AE	437.0	209.0	6.051	0.711878 (7)	0.70517 (9)

[a] Measured values normalized assuming normal Sr with $^{86}\mathrm{Sr}/^{88}\mathrm{Sr} = 0.119400$. Uncertainties refer to the last digit(s) and are two standard deviations of the mean for in-run statistics. Duplicate entries are for a complete replicate analysis where sample numbers are repeated or repeat mass spectrometer run for sample number not repeated.

[b] Calculated ratio for 78 Ma ago with one-sigma uncertainties in the last digits which take into account uncertainties in age (±1 Ma), measured $^{87}\mathrm{Rb}/^{86}\mathrm{Sr}$ (±0.5%) and measured $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ using $^{87}\mathrm{Rb}$ decay constant of $1.42 \times 10^{-11}\ \mathrm{a}^{-1}$.

TABLE VI

Sm-Nd analytical data for Poços de Caldas F4 samples.

Sample	Sm (ppm)	Nd (ppm)	$\frac{^{147}Sm}{^{144}Nd}$	$\frac{^{143}Nd^{a}}{^{144}Nd}$	$\frac{^{143}Nd^{b}}{^{144}Nd \text{ initial}}$
F4 Nepheline syenites					
F4-39-1A	16.53	151.86	0.06581	0.512406 (6)	0.512372 (7)
F4-39-1A	16.38	149.47	0.06626	0.512400 (6)	0.512366 (7)
F4-91-1B	16.30	151.75	0.06494	0.512392 (4)	0.512359 (7)
F4-107-1A	9.554	99.92	0.05780	0.512392 (9)	0.512363 (9)
F4-265-1A	20.11	100.8	0.1206	0.512419 (7)	0.512357 (7)
F4 413 Nepheline syenite xenolith					
F4-413-1A-A	7.315	68.14	0.06489	0.512399 (6)	0.512366 (7)
F4-413-1A-A	6.926	64.14	0.06528	0.512406 (5)	0.512373 (7)
F4-413-1A-C	5.916	56.43	0.06337	0.512401 (5)	0.512369 (7)
F4-414-1A-E	7.466	69.54	0.06491	0.512397 (6)	0.512364 (7)
F4-413-1A-H	5.187	46.60	0.06728	0.512401 (8)	0.512367 (8)
F4-413-1A-L	6.952	65.67	0.06400	0.512399 (7)	0.512366 (7)
F4-413-1A-N	10.61	98.01	0.06545	0.512404 (7)	0.512371 (7)
F4-413-1A-P	10.12	91.33	0.06696	0.512396 (6)	0.512362 (7)
F4-413-1AA	4.305	40.41	0.06442	0.512390 (16)	0.512357 (16)
F4-413-1AC	4.516	39.78	0.06860	0.512390 (17)	0.512355 (17)
F4-413-1AE	10.20	99.53	0.06663	0.512404 (7)	0.512370 (7)

[a] Measured values normalized assuming normal Nd with $^{146}Nd/^{144}Nd = 0.721900$. Uncertainties in the last digit(s), given in parentheses, are two standard deviations of the mean for in-run statistics. Duplicate entries are for a complete replicate analysis where sample numbers are given or repeat mass spectrometer run for sample number not repeated.

[b] Calculated ratio for 78 Ma ago with one-sigma uncertainties in the last digits which take into account uncertainties in age (±1 Ma), measured $^{147}Sm/^{144}Nd$ (±0.1%) and measured $^{143}Nd/^{144}Nd$ using a ^{147}Sm decay constant of 6.54×10^{-12} a^{-1}.

As evidenced from the graph, the F4-413 nepheline syenite samples show a distinct separation from the regional nepheline syenite, which I interpret as indicative of the hydrothermal alteration of regional-like nepheline syenite by a relatively low [Sr] fluid with an $(^{87}Sr/^{86}Sr)_i$ value the same as that of the rock itself. I take this to show that the hydrothermal fluid was equilibrated with the ^{87}Sr of the rock and inherited its ^{87}Sr from that source.

The near-surface F4-NS sample, with marked depletion in Sr, appears to show evidence of extreme weathering. However, slightly lower, but basically unchanged

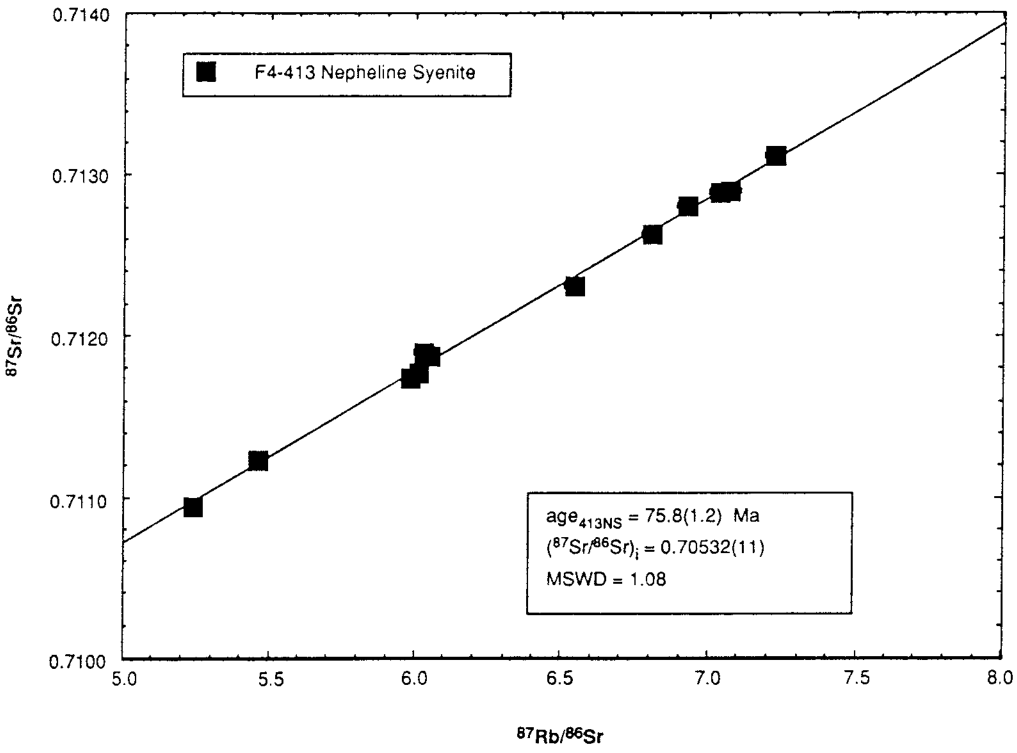

Figure 11. Whole-rock Rb-Sr isochron for Poços de Caldas F4-413 series nepheline syenite. The derived age is 75.8 (1.2) Ma, with an initial $^{87}Sr/^{86}Sr$ ratio of 0.70532(11). The MSWD for the fitted line is 1.08. The well-defined age for these hydrothermally altered samples is interpreted as indicating the age of hydrothermal alteration due to re-equilibration of the Rb-Sr isotopic system.

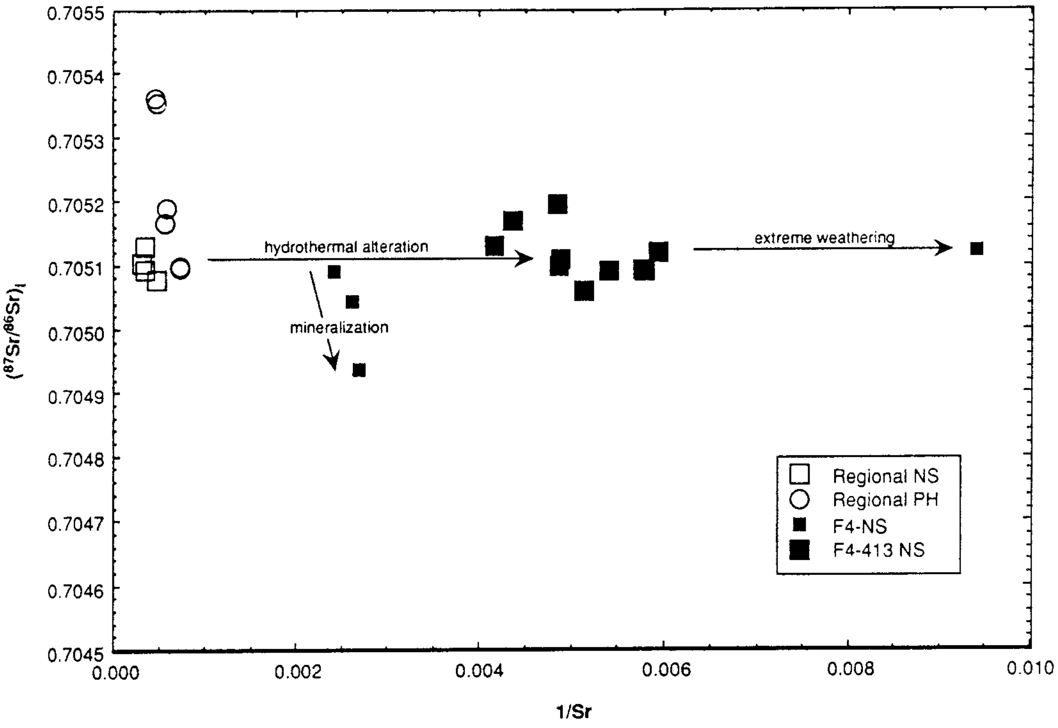

Figure 12. Whole-rock $(^{87}Sr/^{86}Sr)_i$ versus 1/Sr mixing diagram for Poços de Caldas regional nepheline syenite (open squares) and phonolite (open circles), F4 near-surface nepheline syenites (closed small squares) and F4-413 series nepheline syenites (closed large squares). The distinct separation of the F4-413 samples from the regional values is interpreted as indicating alteration by a low [Sr] fluid with an $(^{87}Sr/^{86}Sr)_i$ value inherited from the rock itself. The intermediate F4 nepheline syenite samples show likely evidence of mineralization effects. The lowest [Sr] sample probably indicates extreme weathering effects.

$(^{87}Sr/^{86}Sr)_i$ values of this sample are contrary to a build-up of radiogenic ^{87}Sr, as might be expected for weathering (Bottino and Fullager, 1968; Blaxland, 1974; Brass, 1975; Faure, 1986). The three F4 NS samples intermediate to the regional and F4-413 samples, which are variably mineralized, probably show evidence of mineralization effects. This may be explained by the precipitation of a typical ore gangue mineral such as fluorite. Fluorite (CaF_2) would preferentially incorporate Sr and therefore the $^{87}Sr/^{86}Sr$ ratio of the fluorite would be higher than that of the fluid. This partition coefficient effect would cause an apparent decrease in the initial $^{87}Sr/^{86}Sr$ value.

These samples have had their Rb/Sr ratio changed from approximately 0.05 (regional NS value) to as high as approximately 2.0 (high F4-353 and low F4-413 value) prior to a shift back down to around 1.0 upon weathering, which is mainly due to decreases in the amount of Sr. This elemental change is in agreement with a weathering process explanation, where Rb-bearing minerals (e.g. K-feldspar, micas, clays) tend to be more resistant than Sr-bearing minerals (e.g. plagioclase, apatite, carbonates, fluorite).

It is interesting to note that Kronberg *et al.* (1987) found that, for the direct weathering of "fresh" syenitic rock, the Rb/Sr ratio remained basically unchanged at 5.0, with a reduction of Sr from 110 to 10 ppm and Rb from 500 to 50 ppm.

Once again, the regional phonolite samples exhibit a trend distinct from the other regional and F4 nepheline syenite samples.

Similarly to the Sm-Nd systematics for the regional nepheline syenite and phonolite, the Sm-Nd data of the F4 core samples also cannot be regressed to give any meaningful geochronological information and are shown in Figure 13. Again, however, as for the regional samples, the Sm-Nd data do conform to the calculated model isochron shown, and indicate the same primitive source for the F4 nepheline syenite and phonolite.

It is important to note that the hydrothermal mineralization and metasomatism exhibited in these rocks appears to have disturbed the Sm-Nd systematics. This can be seen in the $(^{143}Nd/^{144}Nd)_i$ versus 1/Nd mixing diagram of Figure 14.

Other studies have compared the effects of hydrothermal alteration on Rb-Sr and Sm-Nd systematics (e.g. McCulloch *et al.* 1980; Jacobsen and Wasserburg, 1979). Both these studies found that the Sr isotopes had been extensively disturbed, while the Nd isotopes remained undisturbed, and for the older (approximately 500 Ma) ophiolites of the Jacobsen and Wasserburg study a precise age and initial ϵ_{Nd} could be determined. Indeed, they found that within the ϵ_{Nd}-ϵ_{Sr} space the rocks displayed an invariant Nd trend that could possibly be explained by a two component mixing trend between the ophiolites and Cambrian seawater.

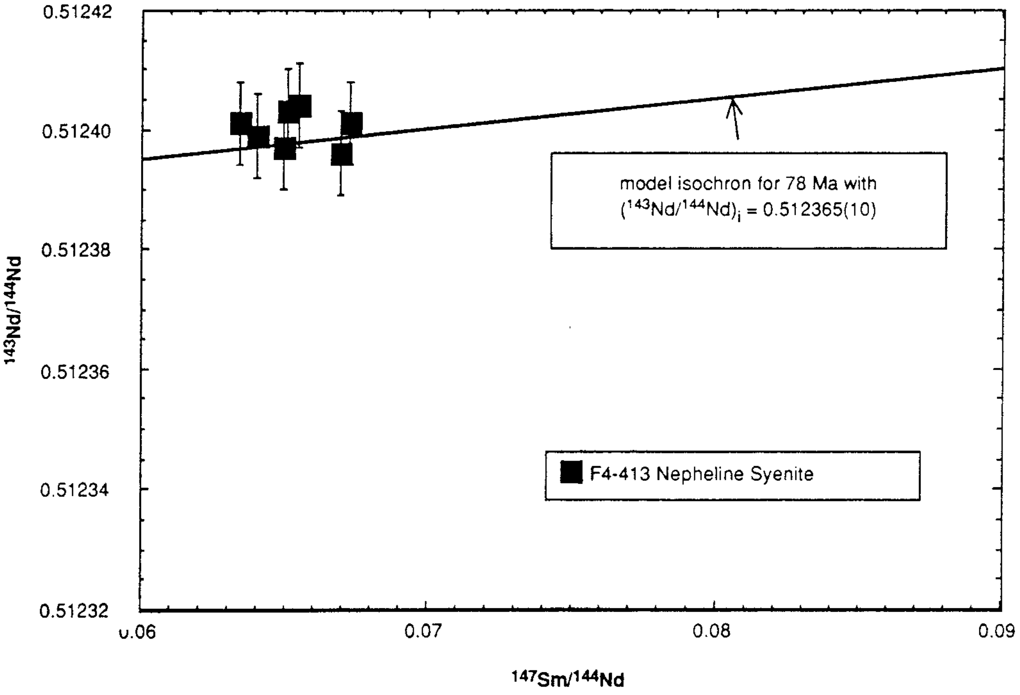

Figure 13. Sm-Nd data for Poços de Caldas F4-413 nepheline syenite samples. Similarly to the regional samples, no geochronological information is extractable from the data, although they do conform to the model isochron.

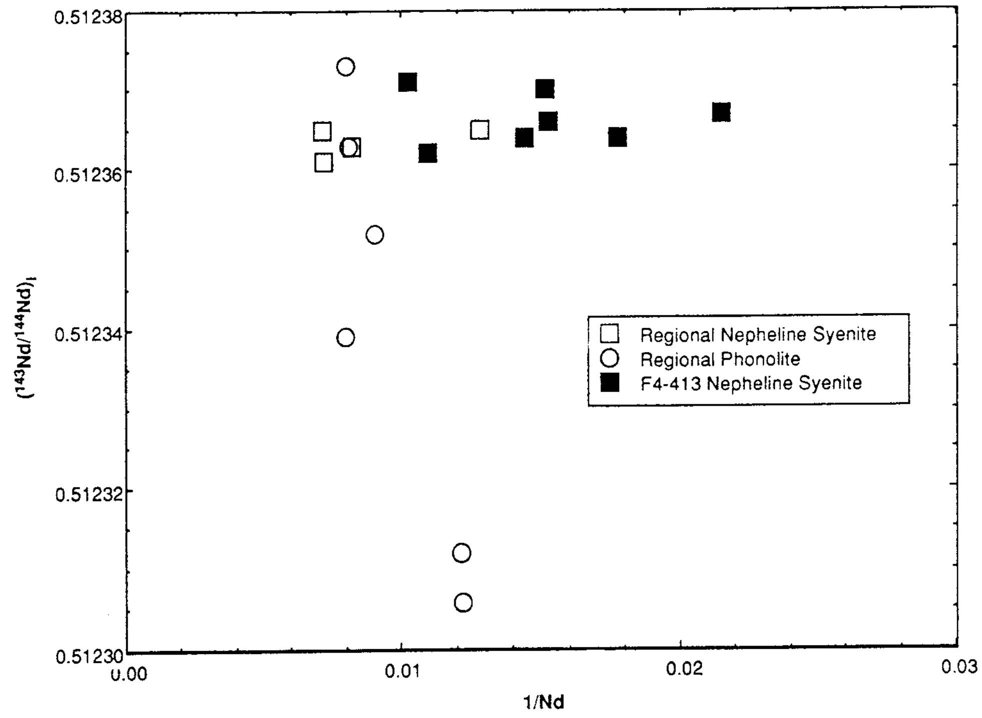

Figure 14. ^{143}*Nd/*^{144}*Nd versus 1/Nd mixing diagram for Poços de Caldas regional nepheline syenites (open squares), phonolites (open circles) and F4-413 nepheline syenite (closed squares). The F4-413 samples appear to have had their Nd isotopic system disturbed by the hydrothermal alteration. The regional phonolites exhibit marked open system behavior.*

I am not familiar with any previously published Sm-Nd studies on hydrothermally altered nepheline syenites or phonolites. Thus, the above observations on the data of this study will hopefully elucidate the effects of hydrothermal alteration on the Sm-Nd systematics of alkaline rocks.

5. Lamproite dyke studies, Osamu Utsumi mine

A shallow-subvolcanic alkaline-mafic dyke crosscuts hydrothermally altered and mineralized phonolites, nepheline syenites and breccias in the open pit of the Osamu Utsumi uranium mine. Two samples, LD-1 and LD-2, from the least altered portion of the exposed dyke, will be discussed in the subsequent sections. Additional locations of the dyke were sampled from morphologically higher benches of the open pit for investigations on supergenic alterations (see Waber *et al.*, this report series; Rep. 2).

Similar rock was intersected in the F4 borehole at a depth interval of approximately 201 m. In spite of the depth, it was significantly altered.

5.1. Petrology

Rock (1987) outlines various criteria and nomenclature for lamprophyres. According to his suggested scheme the term lamprophyre is used as an overall "clan" name, with "branch" subdivisions of: calc-alkaline lamprophyre (CAL), alkaline lamprophyre (AL), ultramafic lamprophyre (UML), lamproite (LL) and kimberlite. Using petrographic and mineralogical evidence as reported in Schorscher and Shea (this report series; Rep. 1) with criteria and associations in Rock (1987), I have tentatively identified and categorized the noted dyke as a lamproite (LL). Specifically, this was based upon: (1) the absence of nepheline or sodalite, (2) the presence of leucite and possibly priderite, (3) the absence of melilite or garnet, (4) the absence of perovskite, (5) the absence of plagioclase, (6) the diopsidic composition and weak zoning of the groundmass clinopyroxenes and phenocrysts, (7) the Ti-rich phlogopitic composition of the groundmass "biotites" and phenocrysts, and (8) the almost pure Fo composition of the groundmass olivines. Although armalcolite and pseudobrookite were not specifically identified, rutile and/or similar Ti minerals occur.

This categorization could be either supported or changed by further mineral chemistry investigations. As it stands, this makes the petrological association of the dyke with the

Poços de Caldas complex an apparently anomalous one, since Rock (1987) finds the association of lamproites with "alkaline rock-carbonatite complexes" to be "unknown". This may be due, however, to a noted lack of South American alkaline complexes and lamprophyres recorded by Rock (1987).

Using major element geochemistry, Waber *et al.* (this report series; Rep. 2), have categorized the mafic dyke as being an ultramafic lamprophyre (UML) according to Rock (1987).

The petrology of the lamproite, discussed in detail in Schorscher and Shea (op. cit.), has three main components: groundmass, phenocrysts and xenoliths. The groundmass contains such phases as clinopyroxene (diopside-hedenbergite), biotite (Ti-phlogopite), glass, opaques and leucite. The phenocrysts contain olivine (torstenite), biotite (Ti-phlogopite) and clinopyroxene (diopside). The xenoliths contain biotite-pyroxenites, pyroxenite, biotites, olivine modules and hydrothermally altered nepheline syenite.

It is important to note that the mineralogical and textural evidence reported in Schorscher and Shea (op. cit.) clearly indicates that the lamproite dyke crosscuts the hydrothermal alteration/mineralization of the Osamu Utsumi mine. This conclusion is supported by preliminary fission-track age-dating performed on apatite separates from the lamproite dyke (pers. comm. N. Waber, 1990). The apatite yielded an age of 95(16) Ma; the high uncertainty is due to a considerable uranium content which has produced a very high track density. Since the apatite gives an age at least as old as the Ar-Ar age, and the tracks in the crystal are not annealed, this indicates that the apatite did not experience temperatures in excess of about 150°C.

5.2. Geochronology

Table VII shows the results of ^{40}Ar/^{39}Ar analyses performed on the lamproite dyke which appears to crosscut the hydrothermal alteration found at the Osamu Utsumi mine. The ^{39}Ar release spectra for two distinct biotite size populations are shown in Figures 15 and 16. The biotite of Figure 15 was collected from phenocryst "books" of approximately 2-4 cm width. The biotite analyzed in Figure 16 was separated from whole-rock samples, with a grain-size of approximately 0.07 mm.

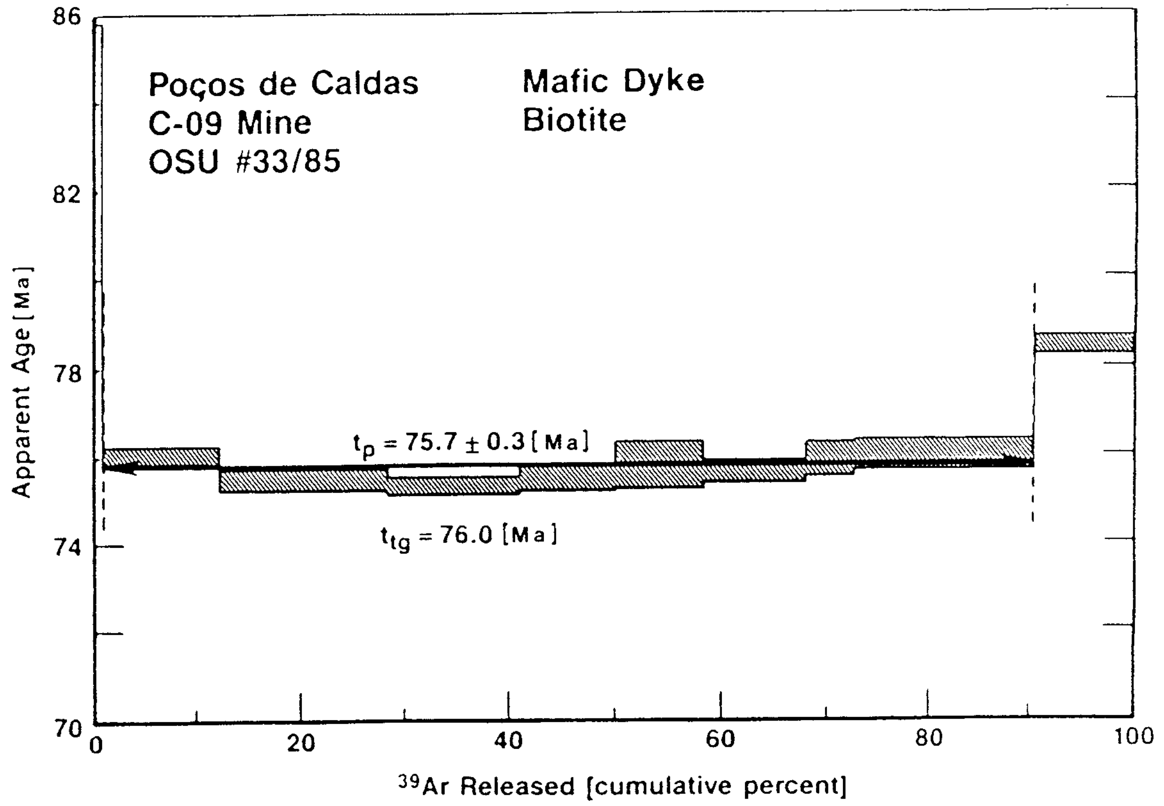

Figure 15. ^{39}Ar release spectra for biotite phenocryst "books" (LD1) from a lamproite dyke exposed in the Osamu Utsumi mine. The dyke is observed to crosscut the hydrothermal alteration and mineralization found within the breccia bodies of the mine. Therefore, the plateau age of 75.7(0.3) Ma for this dyke places an upper limit on the age of hydrothermal activity within the breccia bodies.

TABLE VII

$^{40}Ar/^{39}Sr$ analytical results for Poços de Caldas Osamu Utsumi mine lamproite dyke.

T^a	$\frac{^{40}Ar^b}{^{39}Ar}$	$\frac{^{38}Ar^b}{^{39}Ar}$	$\frac{^{37}Ar^b}{^{39}Ar}$ (X100)	$\frac{^{36}Ar^b}{^{39}Ar}$ (X100)	F^c	$^{39}Ar^d$ (%)	$^{40}Ar^{*e}$ (%)	K/Ca^f	K/Cl^g	APPARENT AGE^h (Ma)
Run #393M (J = 0.007822; 0.0449g)										
FUSE	5.932	0.0207	6.237	0.1314	5.516	100	93.0	8.38	630	76.2 ± 0.8
Run #392L (J = 0.007775; 0.2711g)										
530	8.756	0.0262	19.69	1.587	4.051	2.71	46.3	2.65	470	55.94 ± 2.35
625	6.061	0.0162	29.64	0.1121	5.722	8.76	94.4	1.76	1380	78.52 ± 0.16
685	5.792	0.0176	1.097	0.0572	5.591	12.11	96.5	47.6	970	76.77 ± 0.17
740	5.704	0.0174	0.7543	0.0365	5.564	13.80	97.6	69.3	990	76.40 ± 0.15
800	5.768	0.0169	0.9279	0.0629	5.551	8.95	96.2	56.3	1120	76.22 ± 0.20
850	5.786	0.0164	1.561	0.0722	5.541	16.83	95.8	33.5	1260	76.09 ± 0.18
900	5.807	0.0163	1.775	0.0829	5.531	16.12	95.3	29.4	1290	75.96 ± 0.17
950	6.171	0.0177	2.306	0.2110	5.517	12.16	89.4	22.7	1000	75.77 ± 0.26
1020	7.490	0.0210	32.37	0.6584	5.539	7.85	73.9	1.61	690	76.07 ± 0.33
FUSE	9.331	0.0323	901.7	1.765	4.831	0.71	51.5	0.06	360	66.53 ± 0.86
SUM	6.082	0.0176	13.19	0.1839	5.517	100	90.7	3.96	1020	75.8

^{39}Ar age spectrum: Plateau age, 685°C – 1020°C (87% of ^{39}Ar)	76.2 ± 0.8
Ar isotope correlation regression: 625°C – 1020°C (MSWD = 39; $^{40}Ar/^{36}Ar$ intercept = 283 ± 33)	76.8 ± 0.9

FUSE: Bulk sample is heated and analyzed in a single-step manner. The age derived is equivalent to a K/Ar age determination.

Notes to data in Table VII:

[a] Temperature in °C measured with a thermocouple on the outside of the Ta crucible.

[b] The isotope ratios given are not corrected for Ca-K- and Cl-derived Ar isotopic interferences, but ^{37}Ar is corrected for decay using a half-life of 35.1 days. The ratios are corrected for line blanks of atmospheric Ar composition. The line blanks are approximately: 1×10^{-14} moles ^{40}Ar for T < 1200°C and 2×10^{-14} moles ^{40}Ar for ≥ 1200°C for incremental-heating analyses, and 8×10^{-13} moles ^{40}Ar for total-fusion analyses.

[c] F is the ratio of radiogenic ^{40}Ar to K-derived ^{39}Ar. It is corrected for atmospheric argon and interference using the following constants:

$(^{40}\mathrm{Ar}/^{36}\mathrm{Ar})_{\mathrm{air}} = 295.5$
$(^{39}\mathrm{Ar}/^{37}\mathrm{Ar})_{\mathrm{Ca}} = 6.51 \times 10^{-4}$
$(^{36}\mathrm{Ar}/^{37}\mathrm{Ar})_{\mathrm{Ca}} = 2.70 \times 10^{-4}$
$(^{40}\mathrm{Ar}/^{39}\mathrm{Ar})_{\mathrm{K}} = 0.0329$
$(^{38}\mathrm{Ar}/^{39}\mathrm{Ar})_{\mathrm{K}} = 0.0121$
$(^{36}\mathrm{Ar}/^{38}\mathrm{Ar})_{\mathrm{Cl}} = 2.0175 \times 10^{-6}$ per day after irradiation.

[d] Relative percent of the total ^{39}Ar released by fraction.

[e] Percent of the total ^{40}Ar in the fraction that is radiogenic.

[f] Weight ratio calculated using the relationship: $\mathrm{K/Ca} = 0.523 \times (^{39}\mathrm{Ar}_{\mathrm{K}}/^{37}\mathrm{Ar}_{\mathrm{Ca}})$.

[g] Weight ratio calculated using the relationship: $\mathrm{K/Cl} = 5.220 \times (^{39}\mathrm{Ar}_{\mathrm{K}}/^{38}\mathrm{Ar}_{\mathrm{Cl}})$.

[h] Ages calculated with a λ of 5.543×10^{-10} a^{-1}. Uncertainties are quoted at the 1 σ level. For increments of a step-heating analysis, the uncertainties do not include J value uncertainty. For total-fusion, plateau and other ages, uncertainties reflect a relative uncertainty of $\pm 1\%$ in J value to allow for uncertainty in the age of the monitor. The monitor used was an intra-laboratory biotite with a $^{40}\mathrm{Ar}/^{39}\mathrm{Ar}$ age of 121.7 Ma.

Figure 15 shows that the biotite phenocrysts produce a total gas (t_{tg}) age of 76.0 Ma and a plateau age (t_p) of 75.7(0.3) Ma. As best as can be determined, the exhibited spectra give a plateau, based upon 87% of the released ^{39}Ar gas, which can be interpreted as undisturbed. Therefore I consider the plateau age to be reliable and indicative of the cooling age (at approximately 300°C) of the dyke. The total gas age by the ^{40}Ar/^{39}Ar method is equivalent to a K-Ar age for the same sample.

Figure 16 shows that the finer matrix biotite of the lamproite dyke produces a total gas age of 75.8 Ma and a plateau age of 76.2(0.8) Ma. The release spectra of this biotite population possibly show some indication of disturbance, although I consider it to be very minor. Since it is more likely that this smaller sized biotite population would be more prone to hydrothermal disturbance, the strong agreement between the two age determinations strongly supports the premise, previously based only upon field and petrographic evidence, that this dyke was emplaced subsequent to hydrothermal alteration and primary mineralization.

An average of the coarse and fine biotite total gas ages (76.0 and 75.8) is 75.9 Ma. An average of the coarse and fine biotite plateau ages (75.7 and 76.2) is also 75.9 Ma.

It should be noted that biotite may contain excess ^{40}Ar and still appear to yield plateau-type incremental release patterns (Foland, 1983). An isotopic correlation diagram (see Fig. 16) may elucidate the presence of excess ^{40}Ar (McDougall and Harrison, 1988). The ^{36}Ar/^{40}Ar versus ^{39}Ar/^{40}Ar inverse isochron correlation diagram for biotite sample LD2 yields an age of 76.8(0.9) Ma, a ^{40}Ar/^{36}Ar intercept of 283 ± 33, with an MSWD = 3.9. Considering the high MSWD and large intercept uncertainty, there is no indication of excess ^{40}Ar in sample LD2.

The conclusion that the lamproite dyke was intruded following the primary mineralization at the mine places a very important constraint upon the lower limit of the age of the hydrothermal event(s) as exhibited at the mine. As I noted above in the discussion regarding the Rb-Sr isochron ages of the F4 samples, the Rb-Sr systematics displayed by these hydrothermally altered samples suggest that they have incorporated the age of the hydrothermal alteration. Based upon these considerations, I place a model age of 76(1) Ma upon the lamproite dyke and, in concurrence with the F4 Rb-Sr data, also upon the approximate age of the hydrothermal alteration.

The apparent extreme temporal proximity of the lamproite dyke and the hydrothermal mineralization is quite notable. As indirect support of this conclusion, it has been observed in the study of mesothermal porphyry gold deposits (Rock *et al.*, 1989) that lamprophyric dykes have apparently been emplaced coevally with hydrothermal mineralizing events world-wide, from Archean to Tertiary times.

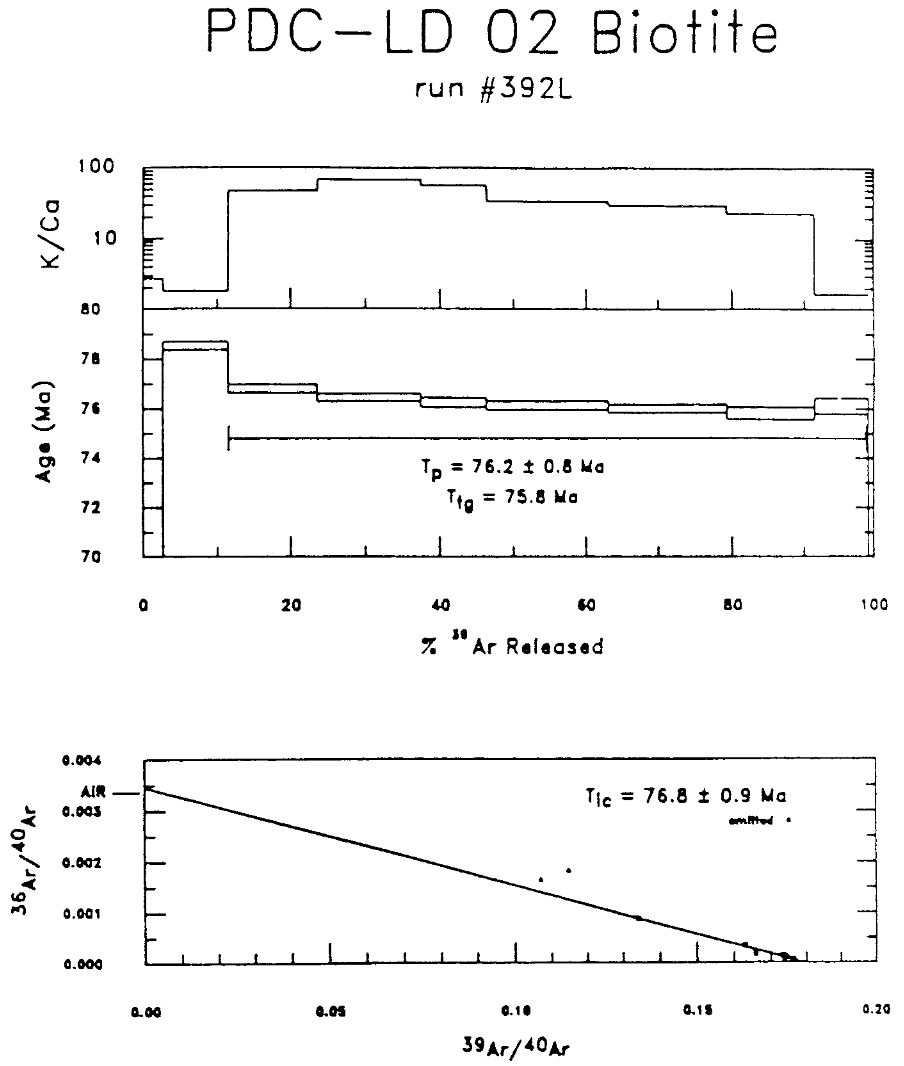

Figure 16. ^{39}Ar release spectra for finer matrix biotite (LD2) from the lamproite dyke of Figure 15. The plateau age of 76.2(0.8) Ma is analytically the same as for the larger biotite population. The ^{36}Ar/^{40}Ar versus ^{39}Ar/^{40}Ar inverse isochron correlation diagram is interpreted as indicating no excess ^{40}Ar.

6. Summary and conclusions

The following conclusions can be drawn from the preceding data and discussions:

6.1. Geochronology

Based upon Rb-Sr analysis of the regional nepheline syenite and phonolite surface samples, the age of the central nepheline syenite, based upon NS-7 mineral separates, is estimated to be 78(3) Ma. By inference, this is assumed to also be the age of the nepheline syenite found at the Osamu Utsumi mine. The age of regional nepheline phonolites could not be determined due to apparent different ages and/or initial $^{87}Sr/^{86}Sr$ ratios for the samples collected, as well as limited data for each of these apparently separate nepheline phonolite bodies.

Based upon Rb-Sr analysis of the F4-NS and F4-413 sample series, coupled with the Ar-Ar analysis of the lamproite dyke found to crosscut the hydrothermal alteration and primary mineralization at the Osamu Utsumi mine, the approximate age of the hydrothermal event(s) that presumably caused the formation of the protore mineralization is estimated to be 76(1) Ma. The age of the mineralization is greater than (based upon petrological evidence), but apparently almost equal to, the age of an intruding lamproite dyke.

It should be noted that the cooling age of the central nepheline syenite is barely, if at all, different to the age of hydrothermal alteration.

6.2. Petrogenesis

The Sm-Nd isotopic systematics of the F4-413 series have apparently been disturbed by hydrothermal alteration or mineralization. This has important implications regarding the retention of these nuclides. Even so, these data do not provide any meaningful temporal information on the crystallization age of the analyzed rocks. However, the primitive nature of the source region of these rocks, which is most likely the partial melt of undifferentiated mantle material, is clearly indicated. As far as I know, this is the first published account of the application of the Sm-Nd technique on nepheline syenites and phonolites, as well as showing both Rb-Sr and Sm-Nd isotopic hydrothermal disturbance.

6.3. Metasomatism

The nepheline syenites and phonolites of the F4 core show a marked enrichment of potassium with a concomitant depletion of sodium and calcium relative to their presumed regional precursors. This enrichment was mainly produced via the precipitation of relatively high K/Na orthoclase, following the dissolution of primary sanidine, albitic plagioclase and relatively moderate K/Na orthoclase.

This hydrothermal metasomatism is the principal cause of the "re-setting" of the F4-413 Rb-Sr isotopic system. This was due to the increase in Rb (and ^{87}Rb) and/or decrease in Sr (and radiogenic ^{87}Sr).

Although metasomatism has been noted as a precursor to alkaline magmatism, these observations are based upon entrained xenocrysts and presumably took place at significant depth (100–200 km). Therefore, even though such a metasomatic process may well have occurred with the alkaline magma source rocks and/or nascent magma, I do not feel that this mechanism can be invoked to be the sole cause of the marked potassium enrichment noted for the Poços de Caldas F4 rocks.

The most reasonable mechanism which would produce the requisite amounts of chemicals, fluids, and volatiles is the circulation of hydrothermal water of meteoric origin.

6.4. Hydrothermal alteration

I interpret the chemical and isotopic changes noted for the F4 Osamu Utsumi mine samples to have resulted from the interaction of regional-type nepheline syenite and phonolite with hydrothermal water of meteoric origin. To presume that these changes are mantle-metasomatic places too great a constraint on the amount of fluid and dissolved elements and volatiles available to produce the marked potassium enrichment observed. This is supported, but not unequivocally proven, by the δD and $\delta^{18}O$ values of the rocks.

The hydrothermal alteration (and metasomatism) was triggered by the formation of breccia pipes through the overlying pile of intrusive and volcanic rock. The cause of this brecciation was the venting of volatiles/volcanics from underlying magma chambers. The driving mechanism of the hydrothermal circulation was the cooling of this underlying body.

The hydrothermal alteration and metasomatism have apparently disturbed the Sm-Nd systematics exhibited in the F4 rocks.

7. Acknowledgements

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