Canadian Mineralogist
Vol. 29, pp. 1043-1050 (1991)

THE TIMING OF ALKALI METASOMATISM IN PALEOSOLS

ANDREW W. MACFARLANE
Department of Geology, Florida International University, Miami, Florida 33199, U.S.A.

HEINRICH D. HOLLAND
Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts 02138, U.S.A.

Abstract

We have measured the concentrations of rubidium and strontium and $^{87}Sr/^{86}Sr$ values of whole-rock samples from three paleosols of different ages. The oldest of the three weathering horizons, the 2,760 Ma Mt. Roe #1 paleosol in the Fortescue Group of Western Australia, experienced addition of Rb, and probably Sr, at 2,168 ± 10 Ma. The intermediate paleosol, developed on the Hekpoort Basalt in South Africa, is estimated to have formed at 2,200 Ma, and yields a Rb–Sr isochron age of 1,925 ± 32 Ma. The youngest of the three paleosols, developed on the Ongeluk basalt in Griqualand West, South Africa *ca.* 1,900 Ma, yielded a Rb–Sr age of 1,257 ± 11 Ma. The Rb–Sr systematics of all three paleosols were reset during post-weathering metasomatism related to local or regional thermal disturbances. The Rb–Sr systematics of the paleosols were not subsequently disturbed. The near-complete removal of the alkali and alkaline earth elements from these paleosols during weathering made them particularly susceptible to resetting of their Rb–Sr systematics. Paleosols of this type are therefore sensitive indicators of the timing of thermal disturbances.

Keywords: alkali metasomatism, paleosol, Precambrian atmosphere, Rb–Sr geochronology.

Sommaire

Nous avons mesuré la concentration du Rb et du Sr, ainsi que le rapport $^{87}Sr/^{86}Sr$, dans des échantillons de roche provenant de trois paléosols d'âge variable. Le plus ancien des horizons lessivés, le paléosol #1 du mont Roe dans le Groupe de Fortescue en Australie occidentale, qui a un âge de 2,760 Ma, a subi un enrichissement en Rb, et probablement aussi en Sr, à 2,168 ± 10 Ma. Le paléosol intermédiaire, développé aux dépens du basalte Hekpoort, en Afrique du Sud, se serait formé il y a environ 2,200 Ma, et donne un isochrone Rb–Sr de 1,925 ± 32 Ma. Le plus jeune des trois paléosols, développé aux dépens du basalte Ongeluk dans le Guiqualand occidental, en Afrique du Sud, il y a environ 1,900 Ma, donne un âge Rb–Sr de 1,257 ± 11 Ma. Dans les trois cas, le système Rb–Sr a été ré-équilibré lors d'une métasomatose tardive reliée à des événements thermiques locaux ou régionaux. Le système Rb–Sr n'a pas été dérangé depuis. Le lessivage quasiment complet des éléments alcalins et alcalino-terreux de ces paléosols pendant la lixiviation a rendu ces paléosols particulièrement sensibles au ré-équilibrage du système Rb–Sr. De tels paléosols sont donc des indicateurs sensibles de l'âge des événements thermiques ultérieurs à leur formation.

(Traduit par la Rédaction)

Mots-clés: métasomatose alcaline, paléosol, atmosphère précambrien, géochronologie Rb–Sr.

Introduction

Paleosols are lithified weathering profiles that can provide information regarding the composition of the atmosphere at the time of weathering. The distribution of iron in paleosols, and possibly that of cerium, may be used as indicators of the O_2 content of the atmosphere during soil formation. The O_2 content of the modern atmosphere is so large that Fe^{2+} released during weathering is usually oxidized quantitatively to Fe^{3+}, and is retained in soils as $Fe(OH)_3$ or Fe^{3+} oxyhydroxides. Under a low-O_2 atmosphere, Fe^{2+} is not oxidized to Fe^{3+}. It is normally washed out of the upper soil horizons, and tends to be reprecipitated as a constituent of one or more Fe^{2+}-bearing minerals in the lower soil horizons, where the pH of soil solutions tends to be higher. Several examples of such soils have been discovered in pre-1,900 Ma terranes (Holland & Zbinden, 1988, Zbinden *et al.* 1988, Holland & Beukes 1990, Macfarlane & Holland 1990).

Intense chemical weathering of basalt in modern environments produces weathering profiles that are strongly depleted in alkali and alkaline earth elements (*e.g.*, Kronberg *et al.* 1987). Such profiles are rich in clay minerals such as montmorillonite, pyrophyllite, kaolinite and gibbsite. By contrast, the well-characterized Precambrian paleosols are highly enriched in K and Rb. Their mineralogy is typically dominated by muscovite. K and Rb are commonly more enriched in the upper parts of paleosols than the immobile elements Al, Ti and Zr, and may be enriched more than ten times over their concentrations in unweathered parent rocks. Residual enrichment alone thus cannot explain the present alkali contents of these paleosols.

Post-weathering introduction of alkali elements by metamorphic or hydrothermal fluids is a much more likely explanation for the elevated K and Rb contents. A similar origin has been proposed for secondary adularia found by drilling beneath an unconformity in Ohio (Faure & Barbis 1983). To test this hypothesis, and to gain further insight into the nature and timing of the transformation of these clay and Al-oxide-rich soils into muscovite-rich metamorphic rocks, we performed Rb–Sr analyses on whole-rock samples of three rather different weathering profiles. Future papers will consider the mobilization of the *REE* during weathering and metasomatism, and the connection between *REE* distributions in paleosols and the oxygen content of the atmosphere.

Description of Samples

The Mt. Roe #1 paleosol is developed on a flow of Mt. Roe Basalt close to the base of the Fortescue Group near Whim Creek, Western Australia. U–Pb dating of zircon has shown that the age of weathering lies between 2,765 and 2,715 Ma (Arndt *et al.* 1990). Weathering probably took place shortly after the onset of basalt extrusion at 2,765 Ma. Unweathered Mt. Roe basalt grades upward into a heterogeneous 3–5 m zone of chlorite-rich rocks, which show evidence of corestone weathering. The chlorite zone grades upward into a sericite- and pyrophyllite-rich zone that is usually about 10 m thick. This zone is strongly depleted in Mg, Fe, Ca, Mn and Na, and is enriched in Al, Ti, Zr and Nb with respect to the parent basalt (Macfarlane & Holland 1990). Concentrations of K and Rb in this zone are much greater than those in the unweathered basalt; they are more enriched than Al and Ti, which were conserved during weathering. The paleoweathering profile is usually overlain by 5–10 m of sediments, mainly fine-grained, ripple-marked siltstones, sandstones and shales, which are in turn overlain by subsequent flows of Mt. Roe Basalt and minor intercalated sediments.

Samples from a paleosol developed on the Hekpoort Basalt in the approach to the Daspoort Tunnel near Pretoria have been described by Hart (1986). The geological setting and chronology of this weathering event were described by Button (1979). At the Daspoort tunnel locality, basalt grades upward into a chlorite-rich zone, which is about 5 m thick. This zone is enriched in Fe and Mn and depleted in Ca and Na relative to the unweathered basalt. The chlorite zone in turn grades upward into a *ca.* 3-m-thick sericite zone that is strongly depleted in Mg, Fe, Mn, Ca and Na. It is enriched in Al, Ti and, especially, in K and Rb over the parent basalt (Hart 1986). The paleosol is overlain by the Dwaal Heuvel Sandstone.

Samples from a paleoweathering profile developed on the Ongeluk Basalt in Griqualand West, South Africa have been described by Wiggering & Beukes (1990). Three episodes of alteration have affected the basalt: an early, subgreenschist-facies alteration, weathering and oxidation, and finally a veinlet-controlled hydrothermal alteration. Weathering appears to have taken place *ca.* 1,900 Ma, and was accompanied by the oxidation and retention of iron. The paleoweathering profile spans a depth of approximately 4 meters. It consists of an upper, oxidized zone and a lower transition zone to unweathered basalt. The transition zone consists of fresh lava with bands of sericite, quartz and hematite. The lower part of the oxidized zone is marked by dark, friable, reddish brown banded, "ferruginized" lava containing abundant hematite, fine-grained sericite and minor chlorite. This grades upward into a massive hematite–sericite zone and a gradual loss of the primary basaltic textures. The oxidized zone is strongly depleted in Mg, Ca and Na. Al and Ti are retained, and K and Rb are enriched relative to the parent basalt. The paleosol is overlain by redbeds of the Olifantshoek Group.

Analytical Technique

Samples of paleosol and parent rock were sawed into 1/2–1 cm thick slabs; the saw marks were then removed by polishing with silicon carbide and alumina abrasives on a clean glass plate. The slabs were cleaned and rinsed repeatedly in deionized water in an ultrasonic cleaner until the water ceased to be visibly turbid. Following cleaning, the slabs were broken into pieces, and chips lacking all evidence of modern weathering were selected. These chips were powdered in a Spex alumina-lined shatterbox; the powders were stored in acid-leached polycarbonate screw-top bottles.

Rb and Sr concentrations and $^{87}Sr/^{86}Sr$ values were determined in the Center for Geoalchemy at MIT. Between 20 and 50 mg of each sample powder was weighed and then spiked with either a mixed ^{84}Sr–^{87}Rb or a mixed ^{41}K–^{84}Sr–^{87}Rb–$^{135-137}Cs$–^{136}Ba spike. Samples were dissolved in a 4:1 HF–$HClO_4$ mixture, dried, and separated using a standard HCl procedure modified from Hart & Brooks (1977). Typical Sr blanks for the complete procedure ranged from 100 to 500 pg; hence, no blank corrections were required. Measurements of isotope ratios were performed on 9-inch and 12-inch radius mass spectrometers at MIT. Sr isotope ratios are normalized to $^{86}Sr/^{88}Sr = 0.1194$, and to $^{87}Sr/^{86}Sr = 0.70800$ for the Eimer and Amend $SrCO_3$ standard. Values of $^{87}Rb/^{86}Sr$ are accurate to better than $\pm 1\%$, and $^{87}Sr/^{86}Sr$ values are accurate to better than ± 0.00004. Regressions of isotope data were calculated using the Isoplot program of Ludwig (1986). All errors in isotope ratios and regression calculations are quoted at the 2σ (95%) confidence level.

RESULTS

Rb and Sr concentrations and $^{87}Sr/^{86}Sr$ values for all samples are shown in Table 1. Seven samples from the Mt. Roe #1 paleosol were analyzed, and the results are plotted in Figure 1. Six of the analyses, including samples from the sericite zone, underlying unweathered basalt and overlying unweathered basalt, fall along an isochron corresponding to an age of 2,168 $\pm$9.7 Ma. One sample from the overlying basalt with a very high Sr concentration was not reset completely during alkali metasomatism and plots slightly above the isochron.

Six samples from the Daspoort Tunnel locality were analyzed, and the results are plotted in Figure 2. Five of the samples were collected from the chlorite and sericite zones of the paleoweathering profile, and plot along an isochron corresponding to an age of 1,925 $\pm$32 Ma. The sixth sample of unweathered basalt, collected from below the weathering zone, falls below the isochron defined by the other samples.

Rb–Sr data for five samples of the paleosol developed on the Ongeluk Basalt are plotted in Figure 3. Three of the samples, those with the

TABLE 1. Rb-Sr DATA FOR WHOLE-ROCK SAMPLES OF PALEOSOLS AND PARENT BASALTS FROM AUSTRALIA AND SOUTH AFRICA

Sample	Sample Description	Sample (mg)	Rb (ppm)	Sr (ppm)	Rb/Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$
Mt. Roe #1 paleosol							
103230	parent Mt. Roe Fm. basalt underlying chlorite zone	26.42	85.05	132.01	0.64	1.875	0.763352
103231	lower sericite zone	19.65	108.13	70.32	1.54	4.512	0.845771
103232	middle sericite zone	29.31	210.88	30.08	7.01	21.646	1.381350
103233	upper sericite	27.44	207.79	119.36	1.74	5.118	0.865918
100534	Mt. Roe Fm. basalt flow overlying paleosol	24.42	15.21	1259.97	0.01	0.0349	0.706431
100535	Mt. Roe Fm. basalt flow overlying paleosol	24.97	25.26	485.93	0.05	0.1505	0.709410
100539	upper sericite zone	25.31	232.43	99.80	2.33	6.881	0.918013
Paleoweathering profile on Hekpoort basalt at the Daspoort Tunnel							
85-ZH-11	middle sericite zone	25.25	267.58	129.62	2.06	6.081	0.887035
85-ZH-13	upper sericite zone	24.97	278.75	151.11	1.84	5.425	0.868493
85-ZH-22	upper sericite zone (highest sample)	24.72	445.09	194.25	2.29	6.762	0.905467
85-ZH-24	lower sericite zone	25.69	336.56	130.41	2.58	7.634	0.928938
85-ZH-18	chlorite zone	24.57	98.91	21.50	4.60	13.835	1.101983
85-ZH-20	parent Hekpoort Basalt underlying weathering profile	45.79	26.99	113.35	0.24	0.6908	0.728814
Paleoweathering profile on Ongeluk Basalt							
733.00	parent Ongeluk Basalt underlying paleosol	49.26	15.08	142.37	0.11	0.3072	0.728506
725.48	lower transition zone	51.66	12.91	216.27	0.06	0.1732	0.734165
724.55	middle transition zone	27.95	56.22	43.06	1.31	3.815	0.802642
723.92	lower oxidized zone	19.95	347.44	20.07	17.31	55.157	1.728569
721.59	upper oxidized zone	23.46	385.62	100.30	3.84	11.383	0.938431

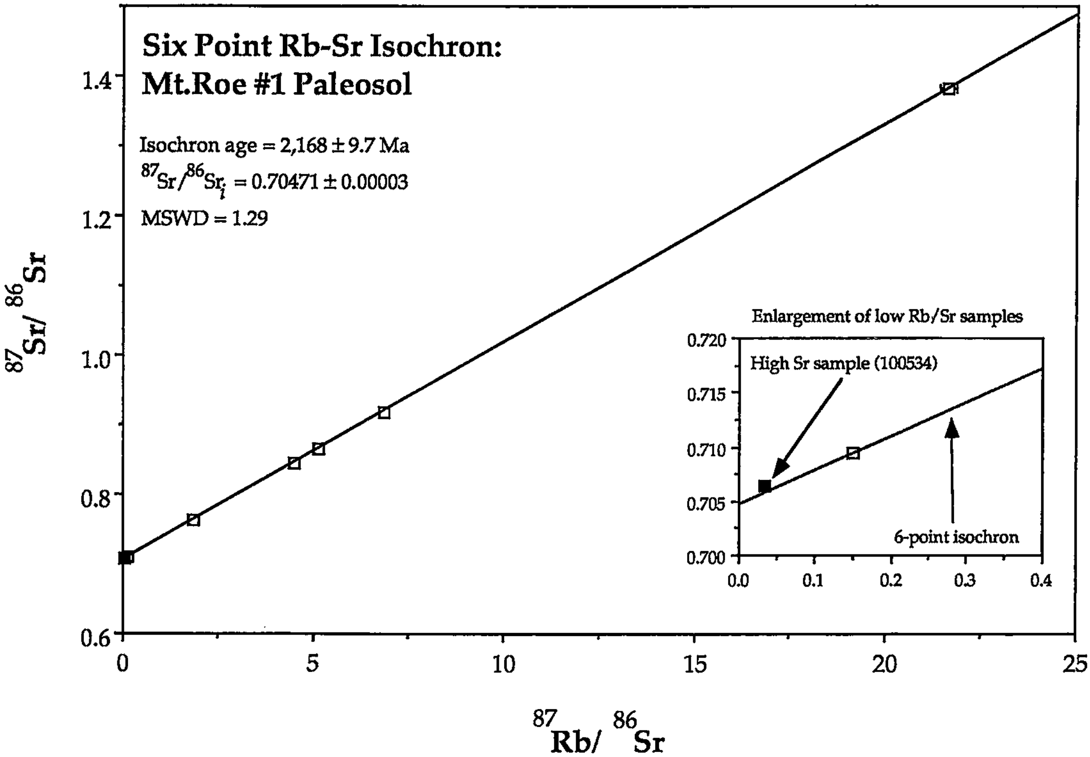

FIG. 1. Six-point Rb–Sr isochron for whole-rock samples of the *ca.* 2,760 Ma Mt. Roe #1 paleosol and over- and underlying basalts from the lower Fortescue Group, Hamersley Basin, Western Australia. The samples with high Rb/Sr were reset by alkali metasomatism; one sample with very high Sr content (1,260 ppm) was not reset.

highest Rb/Sr ratios define an isochron corresponding to an age of 1,257 ±11 Ma. The remaining two samples (see inset) fall slightly off this isochron. However, the age defined by the isochron is not significantly different if all of the points are considered together.

Discussion

Mt. Roe #1 paleosol

The Rb–Sr systematics of the Mt. Roe #1 paleosol indicate that the enrichment of K and Rb in the upper part of the profile, and probably the mild enrichment of Ca and Sr, occurred well after weathering took place. The initial $^{87}Sr/^{86}Sr$ value ($^{87}Sr/^{86}Sr_i$) of this suite of samples, 0.70471 ±0.00003, reflects equilibration of the metasomatizing fluids mainly with the host basalt, and not with older continental material having a high time-integrated Rb/Sr value.

One of the seven samples analyzed was not completely reset during alkali metasomatism, probably owing to its high concentration of Sr. The relatively high $^{87}Sr/^{86}Sr$ and low $^{87}Rb/^{86}Sr$ values of this sample require heterogeneity of $^{87}Sr/^{86}Sr_i$ in the basalt flows at the time of their emplacement. The observation that the Rb–Sr age of the sericite-rich samples from the paleoweathering zone is the same as that of the stratigraphically higher and lower unweathered basalt suggests that the metasomatic event recorded in the paleosol samples is the same event that produced the chloritization and silicification of the Fortescue Group basalts throughout the Pilbara craton.

The time of alkali metasomatism of samples from the Mt. Roe #1 paleosol postdates weathering by at least 530 Ma, and lies within the range of the observed Rb–Sr ages of 2,700–2,000 Ma for whole-rock samples of Fortescue Group basalts summarized by Blake & McNaughton (1984). Recent whole-rock Rb–Sr data on samples of the Mt. Roe Basalt from a drill core located southwest of the town of Tom Price (Nelson *et al.* 1990) yield a scattered isochron corresponding to an age of 2,115 ±447 Ma, and having $^{87}Sr/^{86}Sr_i$ = 0.7061

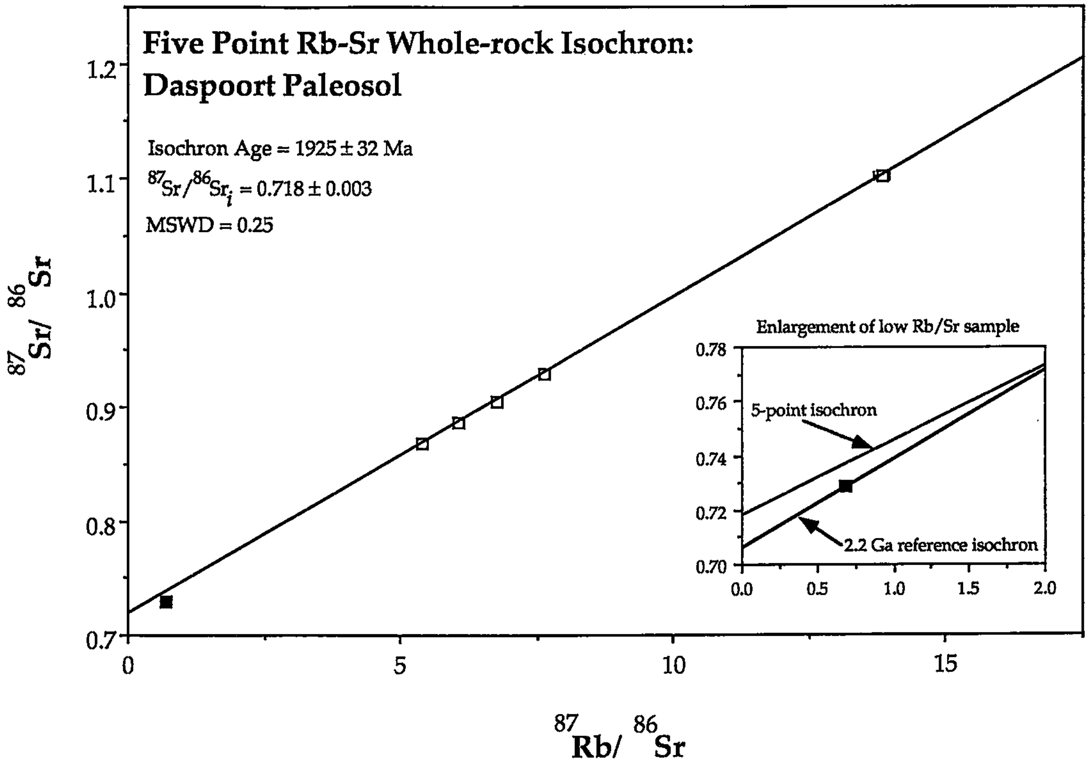

FIG. 2. Five-point isochron for whole-rock samples of a *ca.* 2,200 Ma paleosol developed on the Hekpoort Basalt at the Daspoort Tunnel, near Pretoria, South Africa. Samples with high Rb/Sr were completely reset by alkali metasomatism. The low Rb/Sr sample, an unweathered basalt from the base of the profile, appears to have been only slightly reset and is shown with a reference isochron of 2,200 Ma and $^{87}Sr/^{86}Sr_i \approx 0.707$.

± 0.0006. A Sm–Nd isochron reported for riebeckite from the Hamersley banded iron-formation (BIF) shows that the amphibole grew 2,120 ±32 Ma ago (Alibert & McCulloch 1990). The similarity of the Sm–Nd ages of secondary riebeckite and the Rb–Sr age of the Mt. Roe #1 paleosol suggests that they both reflect a period of low-grade regional metamorphism and metasomatism of the Hamersley and Fortescue groups, which only partly reset the Rb–Sr systematics of unweathered basalts.

Daspoort tunnel paleosol

The Rb–Sr systematics of samples from the Daspoort Tunnel locality also reflect resetting significantly after the time of weathering. The weathering profile is thought to have formed approximately 2,200 Ma (Holland & Beukes 1990, and references therein); the Rb–Sr data indicate an age of 1,925 ±32 Ma. The Rb–Sr age corresponds to the emplacement of the upper granitic members of the Bushveld Complex; the Nebo Granite of the Lebowa Granite Suite is dated at 1,920 ± 40 Ma by the U–Pb (zircon) method (Coertze *et al.* 1978). The alkali metasomatism in the Daspoort Tunnel profile probably occurred in response to hydrothermal activity generated by intrusion of the Bushveld Complex, rather than by a regional metamorphic event. Unlike the unweathered Mt. Roe #1 basalt, the sample of unweathered Hekpoort Basalt falls below the isochron defined by the samples from the weathering profile; its Rb–Sr systematics were probably reset slightly by alkali metasomatism (inset of Fig. 2). An approximate $^{87}Sr/^{86}Sr_i$ value of 0.707 is indicated for the unweathered basalt sample if its Rb–Sr system remained undisturbed after extrusion of the lava.

The $^{87}Sr/^{86}Sr_i$ of the paleosol samples of the Daspoort Tunnel profile is quite radiogenic: 0.718 ±0.003. The metasomatizing fluids must have contained strontium leached from old crustal materials. The most likely source of this strontium is the Dwaal Heuvel Sandstone that overlies the

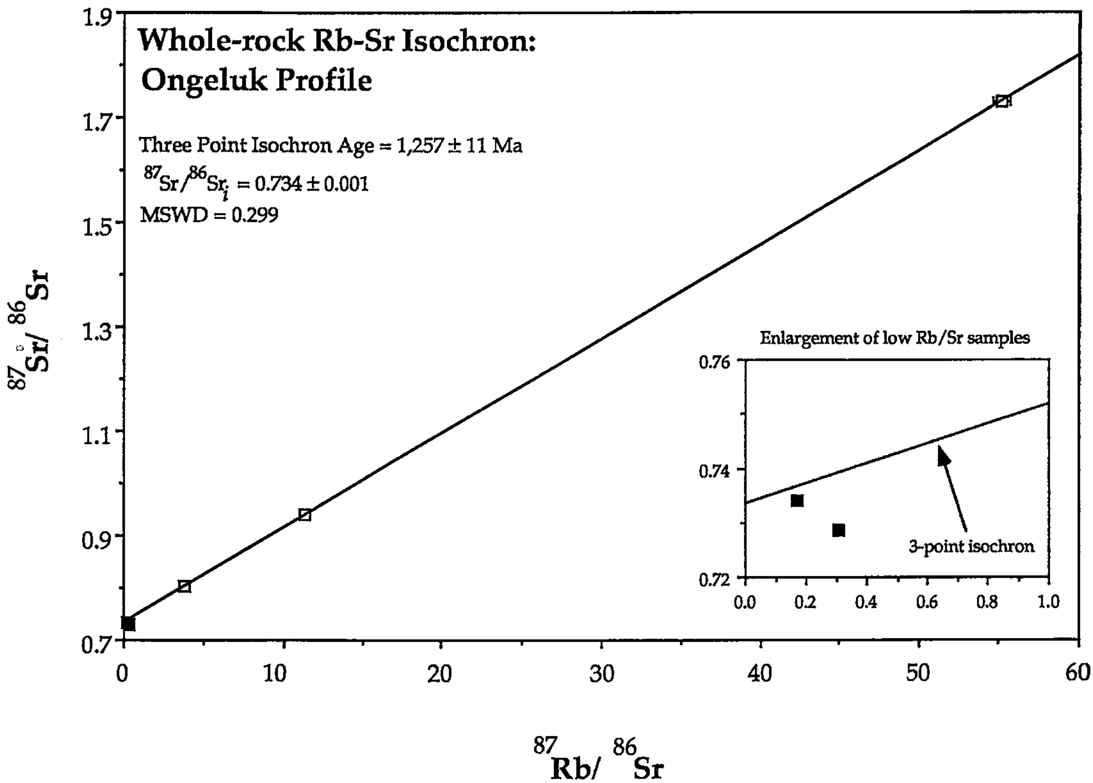

FIG. 3. Three-point isochron for whole-rock samples from a paleosol developed on the Ongeluk Basalt in Griqualand West, South Africa at about 1,900 Ma. The samples having high Rb/Sr were reset by later metasomatism, whereas samples with low Rb/Sr were incompletely reset.

paleosol. The alteration of potassic feldspar in the sandstone could have contributed radiogenic Sr as well as abundant K and Rb.

Ongeluk basalt paleosol

The samples from the weathering profile developed on the Ongeluk Basalt have more complicated Rb–Sr systematics than those of the two profiles discussed above. Three samples from the weathering zone have high $^{87}Rb/^{86}Sr$ values and define an isochron with an age of 1,257 ±11 Ma. This age is identical within the analytical error with a 1,270 ±30 Ma Pb–Pb age for the nearby Kameel mafic intrusive body (Dixon 1988). The alkali metasomatism of the paleosol probably accompanied hydrothermal activity associated with the emplacement of this intrusive body. Field evidence for hydrothermal modification of the paleosol was noted by Wiggering & Beukes (1990). Samples having lower $^{87}Rb/^{86}Sr$ do not conform to the isochron defined by the high $^{87}Rb/^{86}Sr$ samples, and appear to have been variably reset by the metasomatic event. Sample 733.00, the lowest sample and the freshest basalt in the Ongeluk profile, lies furthest from the isochron, whereas sample 725.48 is much closer to the isochron.

Like the paleosol from the Daspoort Tunnel profile, the Rb–Sr systematics of the paleosol developed on the Ongeluk Basalt appear to have been reset by hydrothermal fluids that circulated in response to magmatic activity. Samples from the most intensely weathered part of the paleosol had their Rb–Sr systematics completely reset, whereas less intensely weathered and unaltered basalts were only partly reset, which suggests that fluid flow did not penetrate deeply below the paleosol–Olifantshoek contact. The high $^{87}Sr/^{86}Sr_i$ of the Ongeluk paleosol samples (0.734) indicates that the Sr in the metasomatizing fluids was derived from older, high Rb/Sr material. The sediments in the overlying Olifantshoek Group are a likely source of this Sr.

Conclusions

The Rb–Sr systematics three Precambrian paleosols of differing ages from Australia and South Africa reflect resetting and alkali metasomatism well after the weathering events that produced the paleosols. In the case of the Mt. Roe #1 paleosol, the metasomatism appears to have been related to regional metamorphism and metasomatism in the Pilbara Craton. The Rb–Sr systematics of samples from the sericite zone of the Mt. Roe #1 and from the overlying and underlying basalts have all been reset to a common age; this resetting suggests that fluid infiltration and metasomatism were pervasive. The Rb–Sr systematics of samples from paleoweathering profiles developed on the Ongeluk and Hekpoort basalts appear to have been reset by hydrothermal fluids related to nearby igneous intrusive bodies. In these profiles, the Rb–Sr systematics in samples from the highly weathered parts of the paleosols were completely reset; samples of unweathered and lightly weathered basalt were reset slightly, if at all. The incomplete resetting of the unweathered basalts in the Daspoort and Ongeluk profiles reflects limited hydrothermal flow below the unconformities. The Rb–Sr data indicate that the Sr isotope ratios in the metasomatizing fluids of all three paleosols were homogeneous, and that the Rb–Sr systematics of the paleosols have remained undisturbed either by later circulation of fluid or modern weathering.

Acknowledgements

This research was supported by NASA grant # NAGW-599 to Harvard University. We are grateful to Alec Trendall for alerting us to the existence of the Mt. Roe #1 paleosol and for collecting the initial suite of samples for us. Hubert Wiggering and Nic Beukes shared their samples of the paleosol developed on the Ongeluk Basalt. Stan Hart made his isotope facilities at MIT available, and Ken Burrhus kept it all humming. This manuscript was improved by reviews from Chris Hawkesworth, Robert F. Martin, and a third reviewer.

References

Alibert, C. & McCulloch, M.T. (1990): The Hamersley Basin revisited: the Sm–Nd isotopic systematics of banded iron-formations and associated "shales" and implications for the compositions of early Proterozoic seawater. Proc. Third Intern. Archean Symp. (Perth, Australia), 327-328.

Arndt, N.T., Nelson, D.R., Compston, W., Trendall, A.F. & Thorne, A.M. (1990): The age of the Fortescue Group, Hamersley Basin, Western Australia, from ion microprobe zircon U–Pb results. *In* Correlation of the Fortescue Group (D.R. Nelson, A.F. Trendall & J.R. de Laeter, eds.). *Minerals and Energy Research Institute of Western Australia, Rep.* **82**, Appendix I.

Blake, T.S. & McNaughton, N.J. (1984): A geochronological framework for the Pilbara region. *In* Archean and Proterozoic Basins of the Pilbara, Western Australia: Evolution and Mineral Potential (J.R. Muhling, D.I. Groves & T.S. Blake, eds.). University Extension, University of Western Australia, Perth, 1-22.

Button, A. (1979): Early Proterozoic weathering profile on the 2200 m.y. old Hekpoort Basalt, Pretoria Group, South Africa: preliminary results. *Econ. Geol. Res. Unit, Univ. Witswatersrand, Inf. Circ.* **133**.

Coertze, F.J., Burger, A.J., Walraven, F., Marlow, A.G. & MacCaskie, D.R. (1978): Field relations and age determinations in the Bushveld Complex. *Geol. Soc. S. Afr. Trans.* **81**, 1-11.

Dixon, R. (1988): *Sugilite and Associated Metamorphic Silicate Minerals from Wessels Mine, Kalahari Manganese Field.* M.Sc. thesis, Univ. Cape Town, Cape Town, South Africa.

Faure, G. & Barbis, F.C. (1983): Detection of neoformed adularia by Rb–Sr age determinations of granitic rocks in Ohio. *In* Leaching and Diffusion in Rocks and their Weathering Products (S.S. Augustithis, ed.). Theophrastus Publications, Athens, Greece (307-320).

Hart, S.R. & Brooks, C. (1977): Geochemistry and evolution of early Precambrian mantle. *Contrib. Mineral. Petrol.* **61**, 109-128.

Hart, T.J. (1986): *A Petrographic and Geochemical Study of the 2.2 b.y. Hekpoort Paleosol at the Daspoort Tunnel, Pretoria, in the Republic of South Africa.* A.B. (hons.) thesis, Harvard Univ., Cambridge, Massachusetts.

Holland H.D. & Beukes, N.J. (1990): A paleoweathering profile from Griqualand West, South Africa: evidence for a dramatic rise in atmospheric oxygen between 2.2 and 1.9 b.y.b.p. *Am. J. Sci.* **290A**, 1-34.

______ & Zbinden, E.A. (1988): Paleosols and the evolution of the atmosphere. I. *In* Physical and Chemical Weathering in Geochemical Cycles (A. Lerman, ed.). Kluwer Academic Publishers, Amsterdam (61-82).

Kronberg, B.I., Nesbitt, H.W. & Fyfe, W.S. (1987): Mobilities of alkalis, alkaline earths and halogens during weathering. *Chem. Geol.* **60**, 41-49.

LUDWIG, K.R. (1986): Isoplot200, a plotting and regression program for isotope geochemists, for use with HP series 200 computers. *U.S. Geol. Surv., Open File Rep.* **85-513.**

MACFARLANE, A.W. & HOLLAND, H.D. (1990): Paleoweathering of the Mt. Roe Basalt, Fortescue Group, and the oxygen content of the late Archean atmosphere. Proc. Third Intern. Archean Symp. (Perth, Australia), 289-291.

NELSON, D.R., TRENDALL, A.F., DE LAETER, J.R., GROBLER, N.J. & FLETCHER, I.R. (1990): Isotope systematics and metamorphism of late Archean supracrustal sequences from the Pilbara and Kaapvaal cratons. *In* Correlation of the Fortescue Group (D.R. Nelson, A.F. Trendall & J.R. de Laeter, eds.). *Minerals and Energy Research Institute of Western Australia, Rep.* **82**, Appendix II.

WIGGERING, H. & BEUKES, N.J. (1990): Petrography and geochemistry of a 2000–2200 Ma old hematitic paleo-alteration profile on Ongeluk Basalt of the Transvaal Supergroup, Griqualand West, South Africa. *Precamb. Res.* **46**, 241-258.

ZBINDEN, E.A., HOLLAND, H.D., FEAKES, C.R. & DOBOS, S.K. (1988): The Sturgeon Falls paleosol and the composition of the atmosphere 1.1 Ga BP. *Precamb. Res.* **42**, 141-163.

Received November 28, 1990, revised manuscript accepted August 8, 1991.