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Disturbed Rb-Sr systems of the Archaean Duffer Formation, Eastern Pilbara Block, Western Australia

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Abstract

The Duffer Formation is a thick sequence of Archaean calc-alkaline felsic volcanics in the Pilbara Block. A zircon U-Pb age of 3 453 ± 16 Ma has recently been obtained from this unit (Pidgeon 1978a). However, most Duffer Formation volcanics have been altered and their Rb-Sr whole-rock systems disturbed, indicating ages of between 3 000 and 3 100 Ma. It is likely that a metamorphic event resulted in local isotopic homogenization of Sr at this time.

In this study detailed sampling and description of typical units within the Duffer Formation was carried out to enable the recognition of the least altered lithologies. Samples from McPhee Creek do not define a single isochron but seven samples give an age of 3 018 ± 75 Ma and an initial $^{87}Sr/^{86}Sr$ ratio of 0.701 5 ± 0.000 7, whereas samples from Spinaway Creek define an isochron of age 3 063 ± 114 Ma and initial ratio 0.703 0 ± 0.000 7. However five "least altered" volcanics from McPhee Creek gives an age of 3 471 ± 125 Ma and an initial ratio of 0.699 8 ± 0.000 9. This initial ratio indicates that Duffer Formation magmas were derived from a source with a mantle-like Sr isotopic composition.

Introduction

The origin of early Archaean felsic volcanics is of primary importance to the understanding of Archaean crustal evolution. In many areas of modern felsic igneous activity Rb-Sr trace element and isotopic data provide useful petrogenetic evidence. Unfortunately the mobility of Rb and Sr during hydrous alteration and low grade metamorphism frustrates the interpretation of data from many Precambrian volcanic terrains (e.g. Allsopp *et al.* 1968, Page 1978). This paper presents Rb-Sr whole-rock data obtained during a study of the Duffer Formation, an early Archaean sequence of calc-akaline felsic volcanics in the eastern Pilbara Block (Barley 1980, 1981a).

Recently a zircon U-Pb age of 3 453 ± 16 Ma (Pidgeon 1978a) and galena Pb model ages of between 3 400 and 3 500 Ma (Sangster and Brook 1977, Richards *et al.* 1981) have been obtained from units within the Duffer Formation. However, previous Rb-Sr whole-rock isotopic studies (Pidgeon 1978a, Jahn *et al.* 1981) indicate that post-magmatic alteration processes have involved widespread mobility of Rb and Sr and disturbance of Rb-Sr whole-rock systems. This is reflected by considerable scatter on isochron diagrams (plots of $^{87}Sr/^{86}Sr$ *vs* $^{87}Rb/^{86}Sr$), and regression analyses which indicate ages which are younger than those obtained from zircon and galena studies. Such "isochrons" possess anomalous initial $^{87}Sr/^{86}Sr$ ratios which are of little use in petrogenetic interpretations.

In this study, detailed description and sampling of typical units within the Duffer Formation was carried out to enable the recognition of the least altered lithologies. Analyses of several samples of least altered lithologies within individual units, when compared with analyses of altered lithologies from the same unit, provide an indication of the mobility of Rb and Sr during alteration and the effect this has on Rb-Sr whole-rock systems. The zircon U-Pb age obtained by Pidgeon (1978a) is used as a reference in evaluation of the Rb-Sr whole-rock data.

Area of study

The Pilbara Block is the smaller of the two Archaean crustal blocks in Western Australia. It contains about 56 000 km^2 of granitoid-greenstone terrain, in which metamorphosed volcanic and sedimentary sequences (greenstones) form synclinoria and domes which are separated by large ovoid or elongate batholiths of granitoid and gneiss (Fig 1).

In the eastern Pilbara Block the greenstone sequence is divided into the lower, dominantly volcanic, Warrawoona Group and the overlying sedimentary rocks of the Gorge Creek Group (Hickman 1981). The Warrawoona Group consists of sequences of mafic volcanics interlayered with cherty sediments and sequences of felsic volcanics. The Duffer Formation is a distinctive unit within the Warrawoona Group, composed dominantly of andesite and dacite. It is best developed in the Marble

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Bar Belt, the McPhee Dome and the Kelly Belt (Fig. 1). Studies of the Duffer Formation in the McPhee Dome and the Kelly Belt (Barley 1980, 1981a) indicate that it forms part of a calc-alkaline volcanic association. To the west of the Corunna Downs Batholith (Fig. 1) the Duffer Formation has been dated at 3 453 ± 16 Ma by zircon U-Pb techniques (Pidgeon 1978a). Similar galena Pb model ages of between 3 400 and 3 500 Ma (Sangster and Brook 1977, Richards *et al.* 1981) for the Big Stubby and Lennons Find volcanogenic Zn-Pb sulphide deposits (Fig. 1) support the view that the zircon age is a reliable age of formation.

Metamorphism of the greenstone sequence ranges from prehnite-pumpellyite to amphibolite facies and has been accompanied by varying degrees of strain. Recrystallization of greenstones during low grade metamorphism has resulted in extensive redistribution of many elements and in the formation of mesoscopic zones of alteration or metadomains rich in secondary mineral phases (Barley 1980). Alteration involved

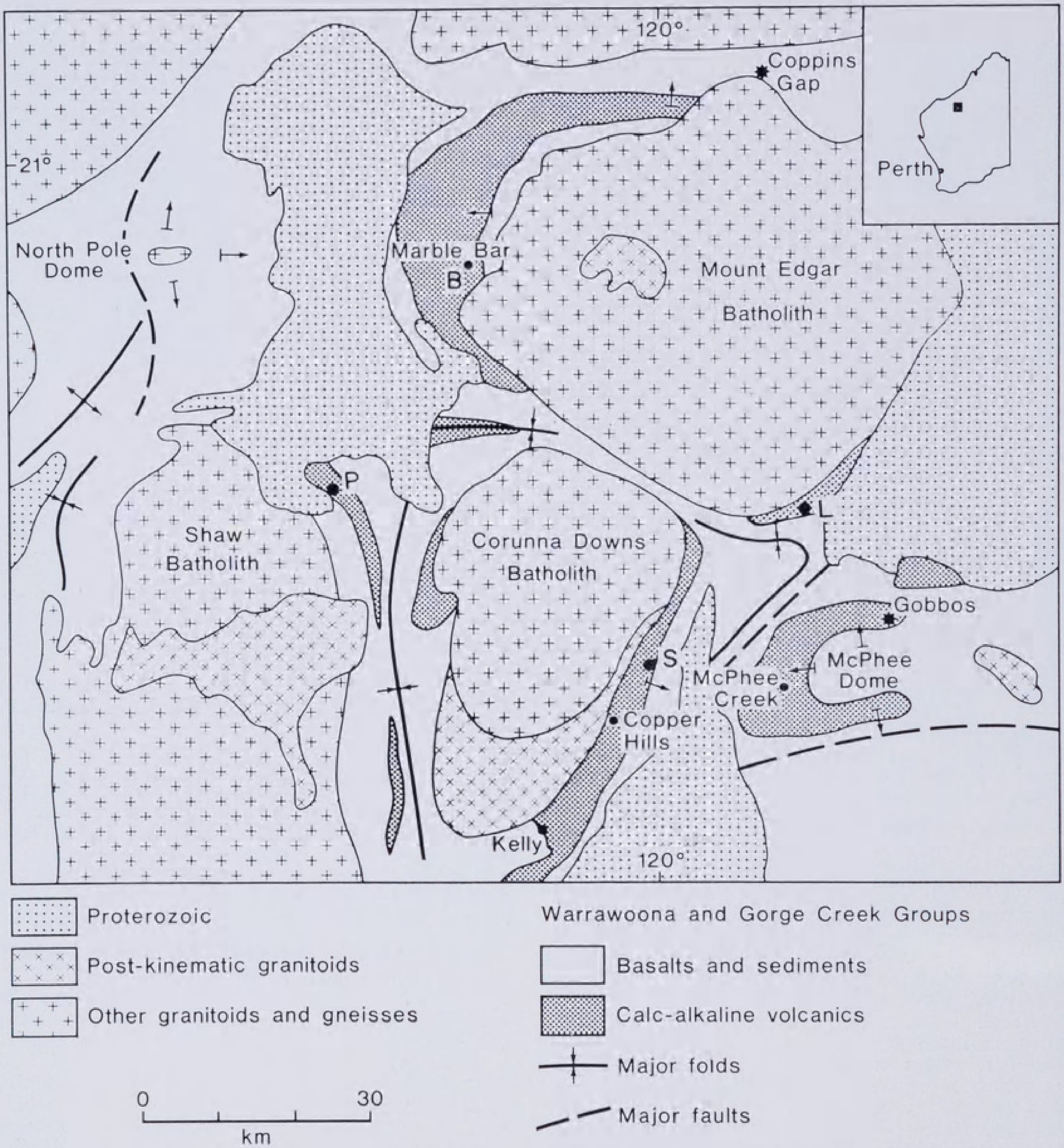

Figure 1.—Geological map of part of the eastern Pilbara Block (after Hickman, 1975, Hickman and Lipple 1975) showing the locations and sample sites referred to in this paper. S = Spinaway Creek, B = Big Stubby, L = Lennons Find, P = Site of U-Pb in zircon study (Pidgeon 1978a). The calc-alkaline volcanic unit includes both the Duffer and Wyman Formations of Lipple (1975).

hydrothermal fluids and is strongest in porous rocks such as pyroclastic units and adjacent to fractures or veins. The centres of massive lava flows and some very large (>30 cm) fragments in pyroclastic units are commonly relatively unaltered, and in areas which have experienced only prehnite-pumpellyite or lower greenschist facies metamorphism may contain relict igneous mineral phases. The style of alteration is also related to the composition of parent rocks. Basaltic and andesitic rocks typically developed metadomains rich in Ca-Al silicate (epidote or pumpellyite depending on metamorphic grade), albite or chlorite and carbonate. On the other hand, Ca-Al silicate metadomains are relatively uncommon in rocks of dacitic and rhyolitic composition where more diffuse albite, sericite and sericite-carbonate alteration is prevalent. Heterogeneous alteration of this type is common in sequences of low grade metavolcanics (Smith 1968, Jolly 1980) and is thought to have occurred during burial. In the eastern Pilbara metadomains can be recognized in greenstones which have subsequently been deformed and metamorphosed to medium or high metamorphic grade (Barley 1981b).

Analytical methods

Depending on grain size, between 0.5 and 1.5 kg of each sample was crushed and approximately 200 g reduced to —200 mesh using a tungsten carbide mill. The experimental procedure for Rb-Sr analysis used in this laboratory are described by Lewis *et al.* (1975) and de Laeter and Abercrombie (1970). The value of $^{87}Sr/^{86}Sr$ for the NBS 987 standard measured during this study was 0.710 2 ± 0.000 1, normalized to a $^{88}Sr/^{86}Sr$ value of 8.375 2. The value of 1.42×10^{-11} yr^{-1} was used for the decay constant of ^{87}Rb. Rb-Sr data are given in Tables 1 and 2. All errors are at the 95 per cent (2σ) confidence limits. Regression analyses of the data were carried out using the program of McIntyre *et al.* (1966).

Table 1

Average Rb and Sr concentrations of least altered volcanics McPhee Dome and Kelly Belt.

	Mafic volcanics (Salgash Subgroup)	Felsic volcanics (Duffer Formation)
No. of samples	37	21
Mean Rb (ppm)	8	32
Range of Rb values (ppm)	1 to 35	4 to 73
Mean Sr (ppm)	113	301
Range of Sr values (ppm)	25 to 340	140 to 563
Average Rb/Sr ratio	0·06	0·11

A method of sampling altered volcanic sequences developed by R. E. Smith and co-workers (Smith 1968, Jolly 1980), which allows, evaluation of element movement during alteration has been used in this study. Alteration patterns in individual units were determined in the field and samples of each type of metadomain were taken, examined in thin section and classified on the basis of their secondary mineralogy (c.f. following discussion and Table 2).

As no samples which completely retained their original igneous mineralogy were found the following criteria (based on the examination of over 200 thin sections) were used when selecting samples of least altered metadomains for analysis:

1) that recognizable igneous textures are well preserved,
2) that secondary mineral phases are restricted to recognizable pseudomorphs after igneous minerals and that secondary mineral assemblages represent the approximate chemical composition of the igneous minerals replaced,
3) that samples contain no monomineralic aggregates of secondary minerals (e.g. epidote metadomains) and were collected as far as possible from inhomogeneities in outcrop, and
4) that samples contain no veins or cavities (e.g. amygdales) and contain less than 2% carbonate (visual estimate).

Where several samples classified as least altered metadomains from a single unit have been analysed, they show little variation in major and trace element contents. The assumption that the concentrations of most elements in least altered metadomains approximate original igneous compositions is also supported by smooth and generally tightly clustered trends on variation diagrams which are consistant with observed petrographic trends (Barley 1980).

For the purpose of this study the Duffer Formation was sampled at McPhee Creek in the McPhee Dome and at Spinaway Creek in the Kelly Belt (Fig. 1). Precise sample locations, descriptions of individual samples and major and trace element analyses are presented by Barley (1980).

Most of the McPhee Creek samples were taken from an outcrop of massive dacite. This unit is grey with diffuse patches (up to 20 cm in diameter) of pink, yellow and dark green coloured metadacite.

The grey metadomains are apparently least altered and show excellent preservation of igneous tectures with phenocrysts of plagioclase (some relict andesine-oligoclase) actinolite (replacing original pyroxene) and rare embayed quartz in a felted groundmass now composed of albite and epidote with minor chlorite and opaque oxides. Samples 86408, 86412 and 86426 are from grey least altered metadomains.

The contacts between grey and pink metadomains are generally quite diffuse (over 2 to 5 cm) and large areas of outcrop have a mottled grey and pink appearance. Pink metadomains contain abundant albite, sericite and carbonate, often partially retaining the textures and mineral assemblages evident in grey metadomains. Abundant carbonate (up to 10%) gives the pink metadomains their distinctive colour. Pink metadomains are enriched in Si, Al, K, Na and Rb relative to grey metadomains and are generally depleted in most other elements. Samples 86418 and 86419 are from pink albite and sericite-rich metadomains.

Yellow metadomains are more sharply defined with mineralogy and texture changing within less than a centimetre. The yellow metadomains are characterized by saccharoidal aggregates of epidote with minor quartz and carbonate. Original igneous

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Table 2

Rb-Sr analytical data for Duffer Formation samples

(i) *McPhee Creek*

Sample	Rb (ppm)	Sr (ppm)	Rb/Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	Sample Type
86424	13	340	0·040 ± 0·001	0·115 ± 0·002	0·70721 ± 0·00051	dacite, yellow metadomain
86435	17	230	0·070 ± 0·002	0·202 ± 0·005	0·71025 ± 0·00012	basalt, least altered metadomain
86412	14	183	0·084 ± 0·001	0·243 ± 0·003	0·71181 ± 0·00009	dacite, least altered metadomain
86408	35	330	0·104 ± 0·002	0·300 ± 0·006	0·71479 ± 0·00022	dacite, least altered metadomain
86409	43	240	0·185 ± 0·003	0·535 ± 0·008	0·72531 ± 0·00025	dacite, yellow metadomain
86426	73	300	0·244 ± 0·004	0·706 ± 0·009	0·73506 ± 0·00018	dacite, least altered metadomain
86413	48	147	0·331 ± 0·003	0·960 ± 0·01	0·74849 ± 0·00019	andesite, least altered metadomain
86419	125	290	0·435 ± 0·008	1·26 ± 0·01	0·75658 ± 0·00031	dacite, pink metadomain
86418	125	280	0·445 ± 0·008	1·29 ± 0·01	0·75815 ± 0·00033	dacite, pink metadomain

(ii) *Spinaway Creek*

Sample	Rb (ppm)	Sr (ppm)	Rb/Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	Sample Type
86456	1·4	195	0·007 ± 0·0002	0·020 ± 0·0005	0·70378 ± 0·00015	basalt, least altered metadomain
86400	35	515	0·067 ± 0·0008	0·194 ± 0·0002	0·71182 ± 0·00019	dacite, least altered metadomain
86363	27	320	0·083 ± 0·001	0·240 ± 0·003	0·71398 ± 0·00016	dacite, least altered metadomain
86402	53	295	0·180 ± 0·002	0·521 ± 0·006	0·72609 ± 0·00021	dacite, least altered metadomain
86405	63	340	0·184 ± 0·002	0·532 ± 0·006	0·72628 ± 0·00025	dacite, least altered metadomain
86407	68	290	0·236 ± 0·003	0·684 ± 0·008	0·73375 ± 0·00022	dacite, least altered metadomain

NOTE: The Rb and Sr concentrations and Rb/Sr ratios have been determined by X-ray Fluorescence Spectrometry. We believe that the values are accurate to ± 5%. The Rb/Sr values do not correspond exactly with the ratios that would be derived from the separate Rb and Sr values listed.

textures are often completely destroyed. Small white patches (1 cm) within metadomains are rich in prehnite. Yellow metadomains are strongly enriched in Ca and depleted in most other elements with the exception of Al and Fe. Samples 86409 and 86424 are from grey metadomains which contain small (up to 2 cm) irregular yellow epidote-rich metadomains.

Sample 86413 is a grey metadomain from an outcrop of massive andesite and sample 86435 a relatively unaltered basalt from the Duffer Formation in McPhee Creek.

The Spinaway Creek samples were taken from the largest fragments (30-50 cm in diameter) in a subaqueous pyroclastic unit (described in Barley *et al.* 1979). With the exception of sample 86456 which is a least altered basalt from a unit overlying the Duffer Formation, all samples are dacites from grey metadomains with textures and mineralogies which are similar to those observed in least altered samples from McPhee Creek.

Results and discussion

Rb and Sr concentrations of volcanics in the McPhee Dome and Kelly Belt (Table 1) are similar to those from other Archaean volcanic sequences (e.g. Hallberg 1972, Hallberg *et al.* 1976, Jahn *et al.* 1974, Arth and Hanson 1975, Hawkesworth *et al.* 1975). Least altered Duffer Formation andesites and dacites have Rb contents which range from 4 to 73 ppm (mean 32 ppm) and Sr contents which range from 140 to 563 ppm (mean 301 ppm) with a mean Rb/Sr ratio of 0.11. Rb-Sr whole-rock data are given in Table 2.

Samples from McPhee Creek do not define a single isochron (Figure 2). Seven samples, including the altered metadomains, form a linear array with MSWD = 1.9. A model 3 isochron fit to these data indicates an age of 3 018 ± 75 Ma with an initial $^{87}Sr/^{86}Sr$ ratio of 0.701 5 ± 0.000 7. The five least altered samples give an age of 3 471 ± 125 Ma, an initial ratio of 0.699 8 ± 0.000 9 with a MSWD of 0.92 This age is similar to that obtained from a

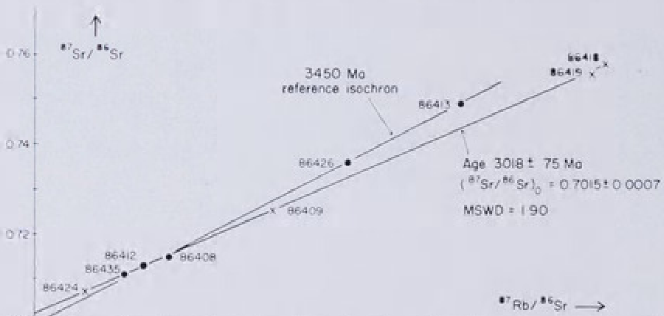

Figure 2.—$^{87}Sr/^{86}Sr$ *vs* $^{87}Rb/^{86}Sr$ diagram for samples from McPhee Creek. ● = least altered sample, x = altered sample.

zircon U-Pb study of the Duffer Formation by Pidgeon (1978a). The initial ratio of 0.699 8 is close to that obtained from other suites of Archaean volcanics and to the value believed to be characteristic of the upper mantle during the early Archaean, (Jahn and Shih 1974, Moorbath 1975, Hart and Brooks 1977). Magmas erupted with initial $^{87}Sr/^{86}Sr$ ratios close to 0.700 0 at this time could have been derived from the upper mantle or by remelting of a short-lived source of low Rb/Sr ratio(e.g. older mafic or ultramafic volcanics). This initial ratio together with the low Rb/Sr ratio of 0.11 preclude derivation of the Duffer Formation magmas by remelting of older sialic crust. Other major and trace element data (Barley 1980) provide objections to mafic or ultramafic eclogite or amphibolite melting hypotheses (Jahn *et al.* 1981), indicating that a process involving fractionation of a mantle-derived mafic parent magma is best able to explain the origin of this suite of felsic volcanics.

Samples from Spinaway Creek (Table 2 and Fig. 3), define an isochron with an MSWD = 0.88 to give an age of 3 063 ± 114 Ma together with an initial $^{87}Sr/^{86}Sr$ ratio of 0.703 0 ± 0.000 7. It is likely that the "secondary isochrons" from McPhee Creek and Spinaway Creek with ages of 3 018 ± 75 Ma and 3 063 ± 114 Ma respectively, are the result of local isotopic homogenization of Sr.

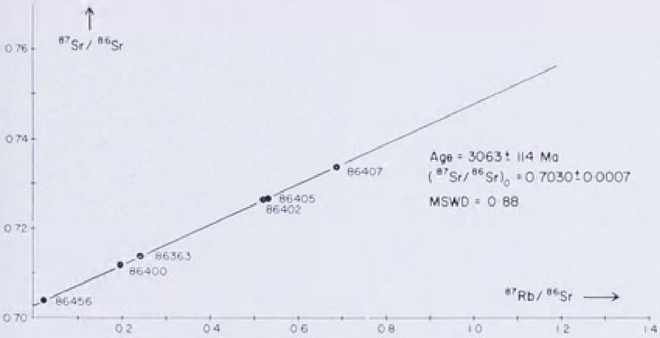

Figure 3.—$^{87}Sr/^{86}Sr$ *vs* $^{87}Rb/^{86}Sr$ diagram for samples from Spinaway Creek.

The Rb-Sr whole-rock systems of many granites and gneisses in the eastern Pilbara also appear to have been disturbed, and commonly indicate ages in the range 2 900 to 3 100 Ma (de Laeter and Blockley 1972, de Laeter *et al.* 1975, Pidgeon 1978b, Cooper *et al.* 1980).

The secondary isochron from McPhee Creek (Fig. 2) includes altered samples from pink sericite-rich metadomains which have anomalously high Rb contents (125 ppm) and Rb/Sr ratios. This observation suggests that the secondary isochrons may have resulted from either:

1. Sr isotopic homogenization during metamorphism and alteration which involved the formation of metadomains or
2. Sr isotopic homogenization (during metamorphism between 3 000 and 3 100 Ma ago) along ^{87}Sr abundance gradients generated by ageing in rocks which had previously been altered (e.g. Cameron *et al.* 1981).

However, because the processes capable of modifying Rb-Sr whole-rock systems are complex and not well understood, the geological significance of these secondary isochrons remains uncertain.

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