ECONOMIC GEOLOGY RESEARCH INSTITUTE
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AN ISOTOPIC STUDY OF FLUORITE RELATED TO THE GRANITES OF THE BUSHVELD COMPLEX

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by

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ABSTRACT

The Lebowa Granite Suite of the Bushveld Complex is a differentiated sheeted intrusion, between 1.5 and 3.5 km thick, with an areal extent of some 30 000 km^2. The granite suite and the overlying Rooiberg Group felsic volcanics are near coeval with the mafic Layered Suite, all being dated within 2057$\pm$3 Ma. Despite this narrow time frame of emplacement ages, a compilation of age dates ranges from 2060 to 1054 Ma and reported $^{87}Sr/^{86}Sr$ are often high and with large uncertainties. Because of hydrothermal alteration, a study of chemical and isotopic variations of the whole rocks is equivocal. Since fluorite has a low Rb/Sr ratio, and is stable at low temperatures, the back correction of the $^{87}Sr/^{86}Sr$ value has minimum uncertainty and the initial $^{87}Sr/^{86}Sr$ of the magma or fluid from which it crystallised can be determined. In this study Rb, Sr, Nd and Sm analyses of fluorite from a number of different types of occurrences are reported. In addition, strontium isotope analyses were made on a 'primitive' granite from a vein cross-cutting the layered mafic suite in the eastern Bushveld and compared to data obtained for an 'evolved' feldspar from the Zaaiplaats granite.

Two distinct processes and events are recognised: (1) a primary magmatic process that occurred at 2057±3 Ma and took place in a very short time span (<1 my) and where hydrothermal fluid was not retained; and (2) a much later secondary hydrothermal process, possibly related to the marginal tectonism of the Kaapvaal Craton in the Limpopo Belt, which may have been a longer-lived event.

The primary fluorite in stockworks, volcanic pipes and disseminated in some granites originated from late magmatic fluid that also infiltrated and engulfed country rock (e.g., Buffalo fluorspar deposit). These fluorites have variable, but low $^{87}Rb/^{86}Sr$, low initial $^{87}Sr/^{86}Sr$ and moderate Sm and Nd (>50 and >100ppm, respectively). The samples from the Vergenoeg Mine have accessory fluorite with low Sr concentrations (32 to 70 ppm), and R_o in the range 0.7166 to 0.7225. Fluorites from the Buffalo, Zwartkloof and Spoedwel occurrences show a wide range of Sr content and R_o, from 39 to 231 ppm and 0.727 to 0.794 respectively, resulting from mixing of a granitic fluid with assorted country rocks. These late magmatic fluids generated large fluorite bodies such as Vergenoeg and had a significant autometasomatic imprint as indicated by chloritisation of biotite such as in the Steelpoort Park granite veins. For the primary fluorite, most samples fall on an array indicating an age of *c*. 2050 Ma, but with a large scatter.

A different and later hydrothermal fluid produced a totally different generation of fluorite and calcite in open vugs and pegmatites at Zaaiplaats and Buffalo. These secondary fluorites display very high R_o, have low abundances of Sm and Nd, with Sm varying from 30.97-0.17 ppm and Nd ranging from 69.59-1.22 ppm. In particular, different coloured fluorite from one pegmatitic pod show an extreme range of initial $^{87}Sr/^{86}Sr$ ratios varying from 0.7199 to 0.8518, with even higher Ro in the calcite.

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AN ISOTOPIC STUDY OF FLUORITE RELATED TO THE GRANITES OF THE BUSHVELD COMPLEX

PREAMBLE

Important deposits of fluorite are spatially and genetically linked to the Lebowa Granite Suite of the Bushveld Complex (Crocker et al, 1988, Martini et al 1991). Some of these such as Ruigtepoort 162 JQ, a lenticular fluorite body in intensely chloritised and haematised Bobbejannkop Granite, have been mined for fluorite in the past (Fig 1.), whereas Vergenoeg on the farm Kromdraai 209 JR is currently a major world producer of acid grade fluorite. Fluorite from various localities around the Bushveld have been studied in an attempt to understand more on the origin of the Bushveld granites and processes of mineralisation.

Figure 1. *Ruigtepoort Mine. Flat lenticular bodies of fluorite+ pyrite, chalcopyrite, arsenopyrite, galena and molybdenite in intensely chloritised and haematised Bobbejaankop granite have been mined for fluorite. The pit has been abandoned.*

INTRODUCTION

The Bushveld Magmatic Province comprises a wide variety of volcanic and plutonic rocks including a mafic Rustenburg Layered Suite, the Lebowa Granite Suite and the overlying Rooiberg Group felsic volcanics, which are all dated within 2057$\pm$3 Ma (Harmer, 2000). The layered suite of the Bushveld Province has well-characterised initial Sr-isotopic signatures and shows a significant crustal input especially in the Main Zone (Kruger, 1990). It is not yet clear if this crustal component is derived from the same or similar source as the Bushveld Granites and Rooiberg Group. Despite the narrow time frame of emplacement, a compilation of age dates shows apparent ages for the granite suite from *c.* 2100 to 950 Ma with a concordant zircon age of *c.* 1950 Ma for late stage mineralisation of a granite (Robb *et al.*, 2000). Reported initial $^{87}Sr/^{86}Sr$ are often high and with large uncertainties. Because of hydrothermal alteration, whole-rock isotopic results give complex isotopic information, and it is not possible to obtain a reliable initial Sr ratio for the granites and felsites.

It is vital to determine the initial isotope character of the granites in order to assess their sources and extent of interactions. Furthermore, knowledge of the initial isotope ratios of the granitic rocks will allow a more rigorous modelling of later isotopic events or processes. The aims of this project were, therefore, firstly, to determine the initial ratios for Sr and Nd of the granite suite at the time of emplacement and, secondly, to assess the influence and timing of later hydrothermal processes that are known to have affected and mineralised the Bushveld granites and overlying volcanic rocks. Two complimentary approaches have been adopted: (1) a granite dyke has been sampled and analysed; and (2) a detailed study of primary and secondary fluorite in the most evolved late granites of the Bushveld Complex was undertaken to assess the initial ratio of the fluorite and the evolution of the secondary fluids. Since fluorite is less likely to have been reset by later fluids than silicate phases, and has low Rb/Sr ratios, the $^{87}Sr/^{86}Sr$ of the fluid from which it crystallised can be determined. Experimental work elsewhere has shown that fluorite is stable under supersolidus conditions and that with low water contents and high fluorine activity, fluorite and biotite are late magmatic phases in granite systems (Webster *et al*., 1987; Sallet *et al*., 2000).

GEOLOGIC SETTING

The Lebowa Granite Suite is a differentiated sheeted intrusion between 1.5 and 3.5 km thick (Molyneux and Klinkert, 1978; De Beer *et al*., 1987; Kleeman and Twist, 1989) with an areal extent of some 30 000 km^2 (Fig. 1). It underlies a sequence of heterogeneous, predominantly felsic volcanic rocks of the Rooiberg Group that are at least 200 000 km^3 in volume, and sills of the Rashoop Granophyre Suite. The granites post-date a 7-8 km-thick layered mafic and ultramafic Layered Suite (Fig. 1), as shown by granite feeder dykes that cut the Layered Suite in the Eastern limb of the Complex (e.g., Hammerbeck, 1970; Walraven and Hattingh, 1993) and xenoliths of mafic rocks in a granite intrusion breccia (Kleeman and Twist, 1989). According to Wilson *et al*. (2000), magnetic foliations and lineations are horizontal, reflecting vertical host-rock compression and horizontal magma flow during emplacement, with space created for the granites by roof uplift and floor depression.

Although early literature (Nicolaysen *et al*., 1958; Burger *et al*., 1967; Davies *et al*., 1970; Hamilton, 1977; Hunter and Hamilton, 1978, and work reviewed in Walraven *et al*., 1990a) indicated that the granites substantially post-dated the Layered Suite, more recent papers have suggested that both extrusive and intrusive Bushveld magmatism occurred within a time span of a few million years (e.g., Kruger *et al*., 1987; Walraven *et al*., 1990a; Walraven and Hattingh, 1993; Hatton and Schweitzer, 1995; Walraven, 1997). This has been confirmed by recent zircon SHRIMP dating on samples from the mafic suite, the Loskop Formation rhyolites, Rashoop granophyres and the Lebowa Granite Suite (Harmer, 2000). This is also consistent with the Pb-Pb evaporation dating of single zircons by Walraven and Hattingh (1993), and recrystallised metamorphic sphene of Buick *et al.* (2001), which indicates that the whole magmatic succession was a quasi-continuous event that happened between *c.* 2061 and 2054 Ma, within the error of the data.

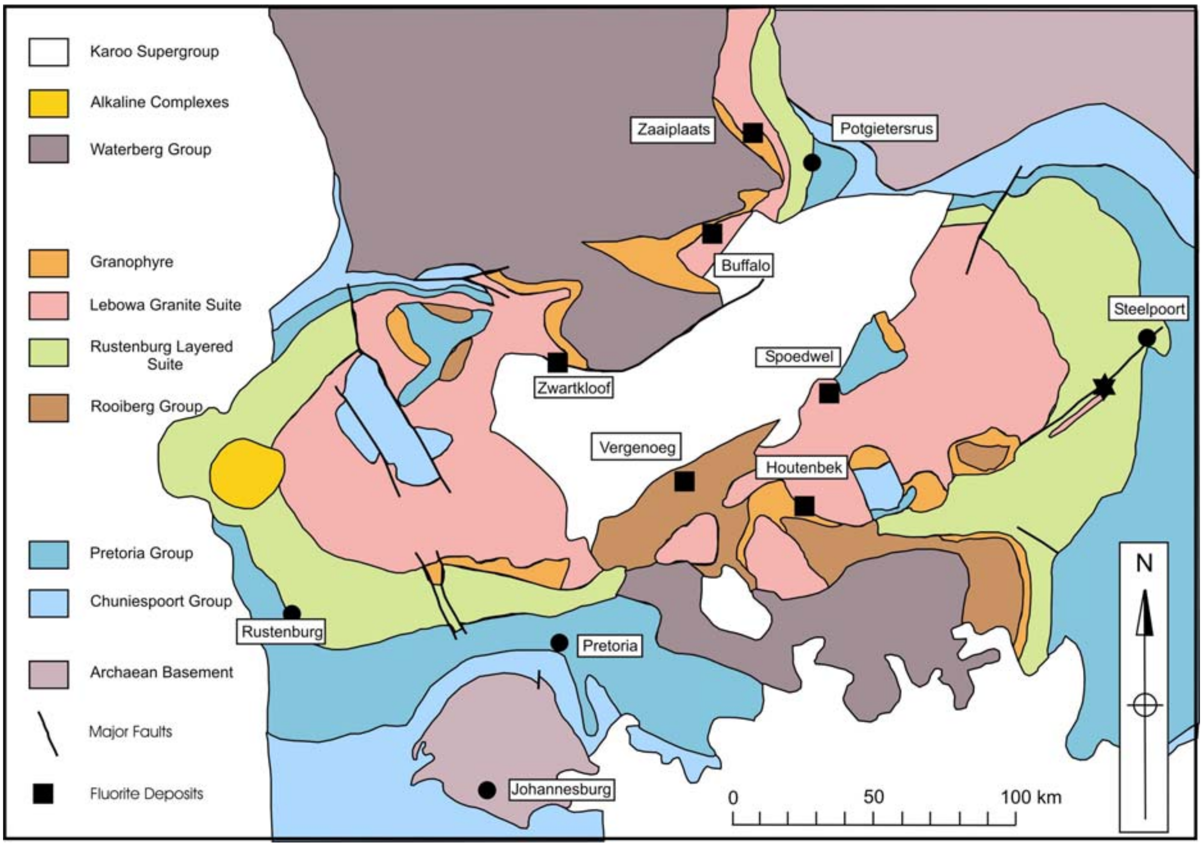


Figure 2. *Map of Bushveld Complex showing localities of fluorite used in this study. The location shown by a star, south of Steelpoort, indicates the position of granite dykes cutting the Main Zone, which were also sampled.*

Compositionally, the granites of the Lebowa Suite are predominantly alkali feldspar granites with iron-rich ferromagnesian minerals and silica contents that generally fall in the range 71-77% SiO_2, with low CaO (0.35- >1%), K_2O/Na_2O ratios >1, and with an upward decrease from the base to the roof of the sheet in Ca, Mg, Ti, P, Sr, and Ba and a concomitant increase in Si, F, Rb, La, Y and Hf. The granites, have many characteristics of A-type granites as defined by Loiselle and Wones (1979), Collins *et al*. (1982), Whalen *et al*. (1987, 1996) and Eby (1990, 1992) and have been categorized as A-type by Kleeman and Twist (1989). Petrographic evidence includes the occurrence of fayalite in the least-evolved facies, and biotite of near end-member annite composition, amphibole of near hastingsite composition (MacCaskie, 1983) and tin and fluorite mineralisation in the most evolved facies. Geochemical evidence includes the relatively low Al, Mg and Ca content, relatively high Fe, F, Cl and HFS elements (Ti, Zr, Hf, Nb and Ta) and low Cr, Co and Ni compared with non-A-type granites having comparable SiO_2. Recent petrogenetic models for A-type granites have involved either extensive crystallisation from mantle-derived magmas (+ crustal assimilation) or partial melting of crustal protoliths and the merits of these models have been extensively discussed in the literature (e.g., Collins *et al*., 1982, Clemens *et al*., 1986; Whalen *et al.*, 1987, 1996; Hill *et al.*, 1996). The $\partial^{18}O$ values for the Lebowa Suite range from +5.9 ‰ to +9.5 ‰, which precludes a predominant pelitic source for the Suite (Hill *et al*., 1996).

The granites of the Lebowa Suite are characterised by many hydrothermal polymetallic ore deposits with an extended paragenetic sequence. An early magmatic mineralisation of Sn-W-F ores, typified by Zaaiplaats Mine, was not associated with large-scale hydraulic fracturing. Rather, fluid circulation was mainly via grain boundaries, microfractures, cavities and dissolution channelways at >600ºC (Pollard *et al*., 1991). A later stage of vein-filling Sn-Cu-Pb-Zn-Ag-Au mineralisation, typified by the Union and Rooiberg Mines, was from fluids at temperatures of 400-200ºC. Late Fe-F-U mineralisation, as at the Albert and Spoedwel Mines, formed from low-temperature fluids at <200ºC (Robb *et al*., 2000).

GRANITE PETROLOGY

The LBS has been subdivided into seven facies (SACS, 1980), with finer-grained variants cutting through or grading into porphyritic types. The Nebo Granite is predominant; the aplitic Lease Granite and the coarse-grained red Bobbejaankop Granite are widespread facies defined largely on colour and texture, whereas the coarse-grained porphyritic Verena Granite, the porphyritic Balmoral Leucogranite, the coarse-grained, locally porphyritic biotite-rich Makutso Granite, and the medium-fine-grained, usually porphyritic Klipkloof Granite of the eastern Bushveld are geographically restricted facies. Only the Nebo and Bobbejaankop granites contain fluorite.

The Nebo Granite typically comprises perthitic alkali feldspar, plagioclase (An_{25}), quartz, hornblende and biotite (MacCaskie, 1983). However, the granite is a sheeted body that grades from a coarse-grained, mesocratic hornblende-biotite granite at the base, or more rarely pyroxene-fayalite granite, through progressively finer-grained, leucocratic, grey, biotite and red granites, often with chloritised biotite, to fine-grained granophyric Lease Granite and granophyre in the roof. However, Hill *et al*. (1996) concluded that the mineralised sheet is not a simple fractionating-upwards sequence. In addition, Wilson *et al*. (2000) suggested that the Nebo Granite in the eastern Bushveld comprises seven different units defined by differences in modal content, crystallisation sequence, magmatic water content, magnetic susceptibility and magnetic fabric.

Figure 3 *Exposures of tin-bearing Bobbejaankop granite at Zaaiplaats*

The Bobbejaankop Granite (Fig. 3) is regarded as a metasomatised tin-bearing roof facies of the Nebo Granite. It is coarse-grained and characterised by brick-red coloured alkali feldspar, occurrence of miarolitic cavities, chloritised mica, disseminated fluorite often intergrown with the mica, and occasional clusters of tourmaline crystals. Alkali feldspars are intermediate or maximum microcline with an increase in the triclinicity as the roof is approached (Lenthall and Hunter, 1977). Hill *et al.* (1996) showed that the Bobbejaankop Granite displays a wide scatter on the Ti *vs* Sc diagram, unlike the regular trend of other granitic rocks, and that on the Ba vs Eu/Sm and Hf *vs* Zr plots the Bobbejaankop Granite appears to be offset from the Nebo trend, which they suggested, is due to metasomatic activity associated with mineralisation.

Many reported initial $^{87}Sr/^{86}Sr$ values of the Bushveld granites are unusually high and with large uncertainties (Davies *et al*., 1970; Hunter and Hamilton, 1978; Hill *et al*., 1996). Conversely, many analyses with high Rb/Sr ratios have impossibly low $^{87}Sr/^{86}Sr$ initial values calculated for ages in the range 1920 to 2050 Ma. Most of these $^{87}Sr/^{86}Sr$ initial ratios are based on whole-rock analyses (e.g., Davies *et al*., 1970; Hunter and Hamilton, 1978; Walraven, 1987, 1988; Walraven and Hattingh, 1993; Hill *et al*., 1996), so samples of feldspar and biotite minerals for this study were collected from a primitive granite dyke.

FLUORITE DEPOSITS AND SAMPLE SOURCES

A number of fluorite deposits are spatially and genetically linked to the Lebowa Granite Suite. Forty-five fluorite localities are noted in the *Mineral Deposits of South Africa* (Martini and Hammerbeck, 1998). Crocker *et al*. (1988) divided fluorite deposits into 4 types:

- Type 1 Zaaiplaats type – fluorite associated with cassiterite in granite
- Type 2 Blokspruit type – fluorite with haematite in granite
- Type 3 Vergenoeg type – fluorite in country rocks
- Type 4 secondary fluorite in the Lebowa Granite Suite (e.g., veins at Zwartkloof and Houtenbek).

Later, Crocker *et al*. (2001) revised this categorization into 4 slightly different types:

- Type 1 fluorite-actinolite-haematite association (Zwartkloof, Buffalo, Vergenoeg)
- Type 2 molybdenite-fluorite-sulphide association (a hybrid of Type 1) (Houtenbek)
- Type 3 cassiterite-tourmaline-fluorite-sulphide association (Zaaiplaats)
- Type 4 sulphide-fluorite-carbonate bodies (Spoedwel)

Samples from six localities (Fig. 1) were selected for this study to reflect different styles of fluorite occurrence. Details of the samples are given in Table 1.

Disseminations in reddened roof facies of granite; Spoedwel and Zaaiplaats

Spoedwel - Fluorite occurs in vugs and disseminations in a brick-red episyenite close to the contact between coarse-grained Nebo Granite and fine-grained granophyre (Fig. 4a). Fluorite is also an accessory in three tabular stratiform massive sulphide ore bodies <5m thick and up to 60 m across, dipping 8ºN and in minor Fe-rich shear-zone-hosted quartz veins (Robb *et al*., 1994).

Table 1 : Details of the fluorite characteristics and geological setting of sample localities

Sample	Locality	Host rock	fluorite sample description
disseminations in reddened roof facies			
SP9	Spoedwel	Close to the contact between coarse-grained reddened Nebo granite and fine-grained granopl	Disseminated purple, appears to have replaced original quartz in an episyenite facies
GC3969	Zaaiplaats	Red miarolitic Bobbejaankop Granite with cassit mineralisation in the roof	Disseminated white-pale purple, associated with cassiterite
GC1723	Zaaiplaats	Pink miarolitic Bobbejaankop Granite associated sulphides	Disseminated pale purple
TM2	Zaaiplaats	Pink altered Bobbejaankop Granite with epidotis feldspars, on the margin of a cassiterite-bearing hydrothermal pipe	Colourless to pale green (rimmed by purple) associated with biotite and chalcopyrite
pegmatitic pods			
LR1	Zaaiplaats	10 cm zoned pegmatitic pod in Bobbejaankop granite; fluorite is zoned with outer rim white or colourless, grading through pale lilac to dark pu with a core of pale or dark green fluorite.	Purple band from zoned fluorite pod
LR2	Zaaiplaats	As above – see Fig. 12	Dark green core of fluorite pod
LR3	Zaaiplaats	As above – see Fig. 12	Colourless outer zone of fluorite pod
LR4	Zaaiplaats	As above – see Fig. 12	Very pale green core of zoned pod
TM1	Zaaiplaats	Large pegmatite body, with coarse quartz (12 cr calcite and fluorite	Purple inner zone
TM3	Zaaiplaats	As above	Colourless outer zone
TM4	Zaaiplaats	As above	Green core
stockworks in Rooiberg felsic volcanics			
GC1673	Zwartkloof	Massive fluorite breccia in Rooiberg felsites	Massive grey-white phase which cements an earlier purple phase
GC1808	Zwartkloof	Brecciated fluorite	Pale purple massive phase cemented by white
stockworks in metasedimentary xenoliths in granite			
GC1670	Buffalo	Fluorite veins in metasedimentary xenolith	White to pale purple
Buf06	Buffalo	As above	Dark purple
Buf07	Buffalo	As above	Massive white
Buf08C	Buffalo	As above	Colourless
Buf08PP	Buffalo	As above	Late pale purple
pipe cross-cutting the volcanic pile			
Ver06	Vergenoeg	Haematite – goethite - fluorite pipe cutting Rooiberg felsites –surface sample	Pale green fluorite associated with haematite
Ver07	Vergenoeg	As above	White fluorite associated with haematite
Ver08P	Vergenoeg	Crackle-breccia with clasts of white fluorite and cement of grey-purple fluorite with sulphides	Pale purple
Ver08W	Vergenoeg	As above	White
Ver11	Vergenoeg	Bulk plant fluorite product	Ochre-coloured bulk
Ver38/440	Vergenoeg	Thin fluorite veinlets in core 38 from 440 m dep	White fluorite in Rooiberg felsites
Ve124/472	Vergenoeg	Disseminated with fayalite, magnetite in core from 472 m depth	White fluorite, associated with silicates and Fe oxides
pipe cross-cutting granite			
HBL21	Houtenbek	Fluorite - molybdenite - quartz - sphalerite vein f breccia pipe in granite	Massive white to pale purple in early vein set

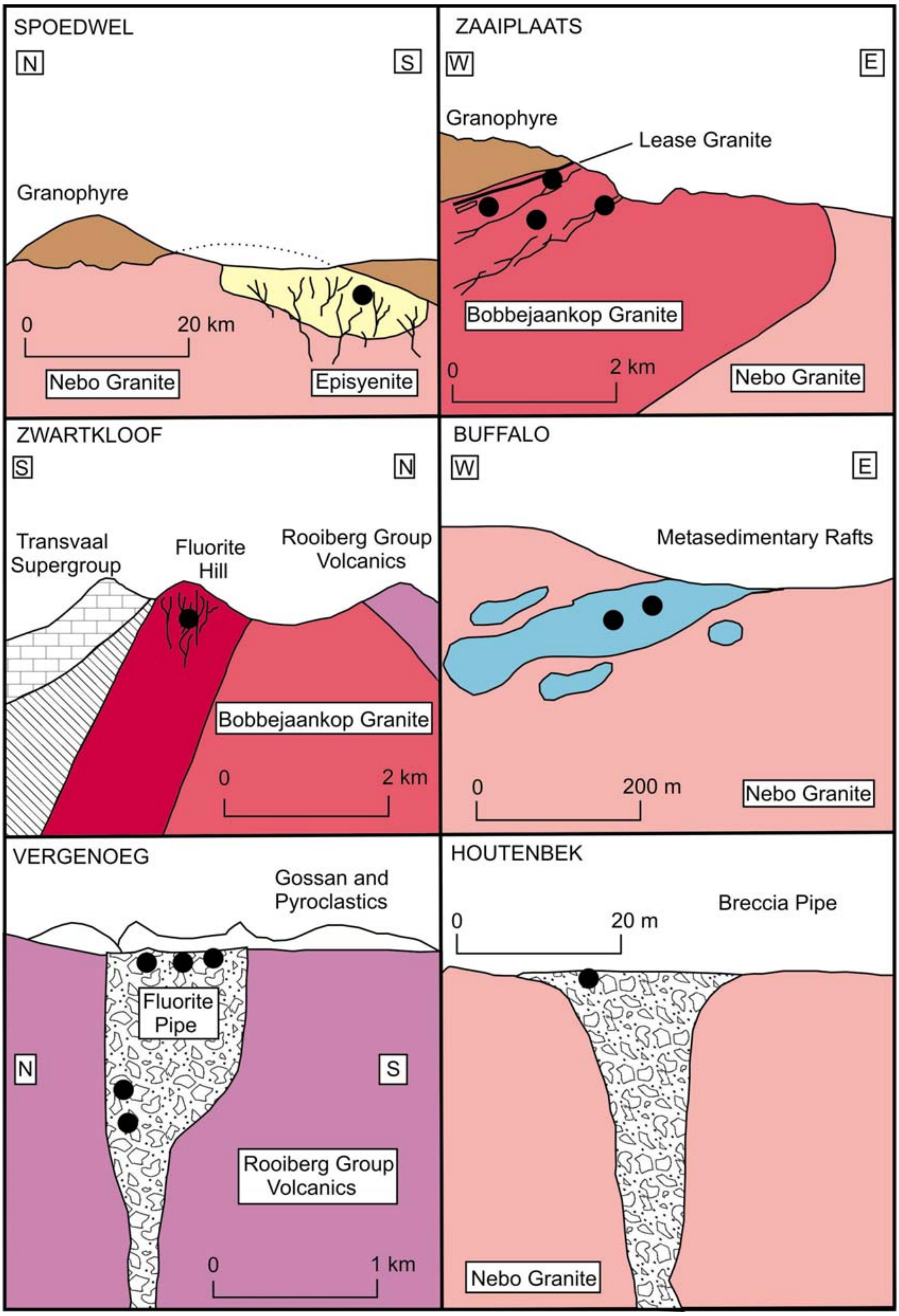


Figure 4. *Sketch sections of the different type of fluorite deposits: (a) Spoedwel, based on a composite for Albert and Spoedwel deposits (after Robb et al., 1994); (b) Zaaiplaats (after Pollard et al., 1989); (c) Zwartkloof (after Pringle,1986); (d) Buffalo (after Absolom,1986); (e) Vergenoeg, based on internal mine cross-sections; and (f) Houtenbek (after Freeman, 1998). Dots mark the approximate locations of samples.*

An almost vertical stockwork of quartz-fluorite veins with chalcopyrite, pyrite, sphalerite, galena and arsenopyrite is interpreted as feeder veins to the stratiform ore bodies (Robb *et al*., 2000).

Zaaiplaats - Bobbejaankop Granite predominates, with pale-coloured aplitic Lease Granite immediately beneath the Rashoop Granophyre (Fig. 4b). Accessory fluorite and cassiterite are disseminated in the red miarolitic roof facies of the Bobbejaankop Granite (Fig. 5) and in hydrothermal pipe-like ore bodies that cut the Bobbejaankop Granite and overlying Lease Granite (Pollard *et al*., 1989).

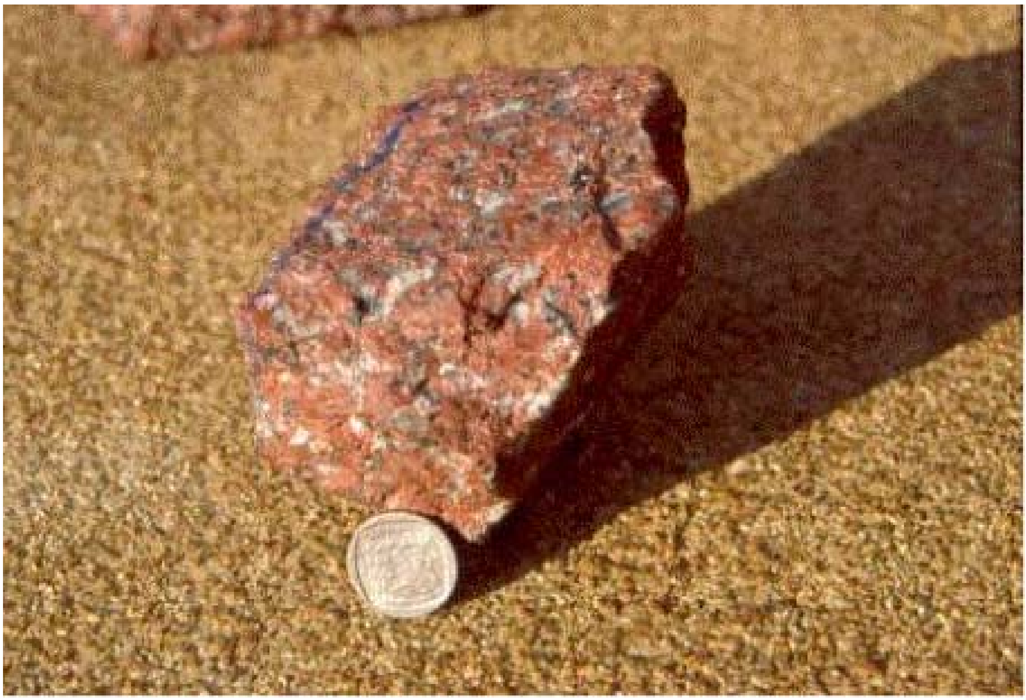


Figure 5. *Red Bobbejaankop granite with accessory purple fluorite, Zaaiplaats*

Pegmatitic pods associated with Sn mineralisation in granite roof facies; Zaaiplaats

The Lease Granite is separated from the Rashoop Granophyre above by fluorite-bearing pegmatites. In both the Lease and Bobbejaankop facies (Fig. 4b), interstitial fluorite occurs in pegmatitic pods and miarolitic cavities with large quartz crystals and more rarely euhedral calcite. Coarse fluorite may show a well-defined to diffuse zonation of colours, typically with a white or colourless fluorite rim, grading through a pale lilac, into a dark-purple zone, and sometimes with a core of pale or dark-green fluorite. Associated quartz crystals may be zoned with clear cores and milky overgrowths. Fluorite from coarse pegmatite and miarolitic fluorite were prepared for this study; four samples of different colours from a 10 cm zoned fluorite pod, and three other samples of different colours from very coarse pegmatite, together with pink calcite were selected (Fig. 6 and Table 1).

Figure 6. *Coarse pegmatite with pink calcite (centre), euhedral clear quartz (bottom right) and purple fluorite (top right), Zaaiplaats.*

Stockworks in Rooiberg felsic volcanics; Zwartkloof

Three fluorite bodies are located at the intersection of west-northwest and an east-west fracture system in Rooiberg felsites (Pringle, 1986). Veins in felsite (Fig. 4c) comprise fluorite, siderite and ankerite, with minor pyrite and sphalerite. The fluorite varies from massive to granular, is commonly brecciated and varies from light green, white or blue to purplish, with brown iron-oxide staining on cleavage planes. More than one generation of fluorite occurs in some of the veins, with pale-purple fluorite cemented by white fluorite. A thin selvage of quartz, 1-2mm thick, separates the fluorite breccia from the felsite itself. Samples of purple fluorite clasts and the later white fluorite cement were separated for analysis (Table 1).

Stockworks in metasedimentary xenoliths in granite; Buffalo

A stockwork of fluorite veins, ranging from <1 mm -150 mm, and averaging 10 mm in thickness, are subparallel to the relic bedding within xenoliths of Transvaal Supergroup metasediments (known as leptite) in the upper part of the Nebo Granite (Fig. 4d). Fluorite also occurs at the contact between granite and metasediment and along joints in granite (Fig. 7). The fluorite varies from dark purple to pale green, yellow and colourless. Chlorite is the principal gangue with accessory monazite (Absolom, 1986). Six different coloured samples from discontinuous veinlets of fluorite in the xenolith were selected for analysis (Table 1).

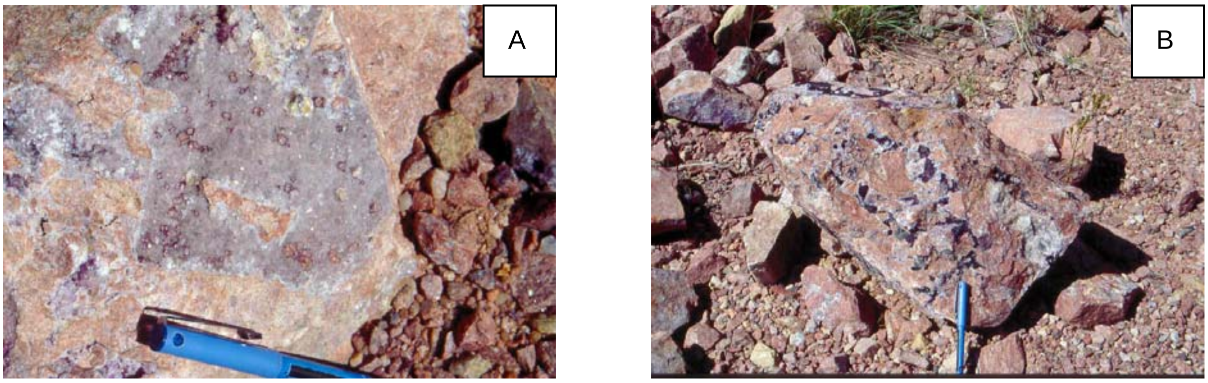


Figure 7. *Fluorite from Buffalo South Pit (a) fluorite at contact between granite and metasediment; (b) fluorite along joint planes in granite*

Pipes cross-cutting the volcanic succession; Vergenoeg

Fluorite is a major component of the funnel-shaped, iron-rich Vergenoeg pipe in Rooiberg felsites (Fig. 4e). The pipe is surrounded by stratiform haematite-fluorite breccias within the felsic pyroclastic sequence (Crocker, 1985) (Fig.8). The pipe, which is 900 m in diameter at the surface, tapers to 700 m across, at least 600 m in depth and appears to lack any alteration envelope. The pipe is zoned vertically; a 50 m surface cap of gossan and pyroclastics consisting of fluorite, haematite and goethite overlies an assemblage of fluorite, magnetite, haematite, siderite, stilpnomelane and apatite with accessory pyrite, chalcopyrite, sphalerite, arsenopyrite, molybdenite and galena to a depth of 300 m. Fluorite comprises 25-30% of this assemblage. Beneath this, fluorite is less abundant in an assemblage of ferroactinolite after fayalite, Ti-magnetite, minor apatite, pyrrhotite, arsenopyrite and lőllingite. The unoxidised mineral assemblage at depth comprises fayalite and Ti-magnetite, with minor pyrrhotite and fluorite. In the southwestern part of the open pit, a small plug of crackle-brecciated fluorite, approximately 25 m in diameter, cuts the main pipe. Clasts of grey-white fluorite are cemented by fluorite and iron oxides (Fig. 9) with accessory pyrite, chalcopyrite, sphalerite, arsenopyrite, molybdenite and galena. Surface samples of different-coloured fluorite were collected from the open pit, including material from the crackle-breccia. Samples from borehole core were selected to include thin fluorite veinlets in volcanic country rocks (at a depth of 440 m), and a sample of disseminated fluorite from the fayalite-bearing assemblage (at 472 m depth). A sample of refined fluorite from the mill was also collected to represent a bulk sample from recent mining.

Pipes cross-cutting granite; Houtenbek

Fluorite occurs both in veins in altered granite and in country rock xenoliths hosted by a small breccia pipe, 15-20 m in diameter, which cuts the Nebo Granite (Fig. 4f). The pipe has been mined out so field relationships are not clear, but rubble on the spoil heap indicates that blocks of granite and metasedimentary xenoliths were cemented by a fluorite breccia (L.J. Robb, pers. comm.). Both the granite and metasedimentary blocks are hydrothermally altered and may contain veins of fluorite with accessory molybdenite and other minerals. The sample analysed, HBL21, is of fluorite breccia with colourless fluorite crystals typically 15 mm across cemented by white and some purple fluorite with ragged sheaves of accessory molybdenite 25 mm in length (Fig. 10).

Figure 8. *Vergenoeg fluorite Mine, looking ESE across the pipe to the felsic pyroclastic sequence in the background.*

Figure 9. *Crackle breccia in Vergenoeg open pit showing clasts of grey-white fluorite in a haematite-fluorite matrix*

Figure 10. *Sample HBL 21 from Houtenbek comprises a fluorite breccia with colourless fluorite clasts cemented by white-purple fluorite with accessory molybdenite*

In summary, there are two types of fluorite genetically linked to the Lebowa Granite Suite. The first type is a disseminated fluorite intergrown with biotite in the Nebo and Bobbejaankop Granites, or associated with fayalite or ferroactinolite in the Vergenoeg pipe. These fluorites are regarded as primary and are likely to be synmagmatic at 2057 ± 3 Ma. The other type is a later post-magmatic fluorite that may be associated with a subsequent hydrothermal episode and which we regard as secondary. This fluorite is not expected to provide a reasonable estimate of the initial ratio, but does provide constraints on the process and timing of hydrothermal alteration.

The sample source for the ‘primitive’ granite was from a thin dyke, 20-30 cm thick, in the eastern Bushveld Complex. It occurs in the Steelpoort River Valley, north of the Steelpoort Park Granite (Hammerbeck, 1970), cutting the Main Zone of the Rustenburg Layered Suite 20km south of Steelpoort (shown by a star in Fig. 2). Contacts with the host are sharp and there is no evidence of hydrothermal alteration in the two-pyroxene gabbro. Hence, we suggest that this granite dyke may not have been subjected to the pervasive alteration that causes complications in interpreting isotopic systematics in the main granite bodies. The feldspars are white to pale-pink perthite, but the accessory biotite (1-2%) is chloritised. In addition, a sample of microperthite was separated for analysis from the red Bobbejaankop Granite at Zaaiplaats (Fig.2).

SAMPLE PREPARATION AND ANALYTICAL PROCEDURES

For coarse-grained fluorite samples, individual grains were collected directly from the rock, crushed to +250 mesh sieve size, and cleaned by handpicking under a binocular microscope. For pegmatitic samples from Zaaiplaats, different coloured fluorite grains from a zoned pod were carefully hand picked and processed separately. For samples with disseminated fine-grained fluorite and for the granite dyke, rock samples were split, crushed and sieved. Fluorite was hand picked under a binocular microscope from the +125, -150 mesh sieve fraction. For the granite sample, separates of plagioclase and biotite were also hand picked under a binocular microscope from the -125 +90 mesh sieve fraction.

Samples were washed and the pure mineral samples were then crushed to fine powder in an agate mortar for analysis. Each sample was weighed into Savillex™ beakers, and spiked prior to dissolution. Spikes used were ^{84}Sr (99%), 99% Rb, and ^{149}Sm and ^{150}Nd. Dissolution in 6M HCl-7M HNO_3 of the first batch of fluorite samples proved to be extremely slow, so a borax-HNO_3 mix was successfully used to digest the second batch of samples. After dissolution, the liquids were evaporated to dryness and acidified with ~5ml HCl to form a chloride salt. Bulk separation of Sr and REE's was achieved by standard cation-exchange chromatography techniques in quartz glass columns with Bio-Rad AG50W 8x200-200 mesh cation exchange resin. Separation of Nd and Sm from the REE fraction was undertaken in 8 x 0.8 cm Teflon columns with Teflon powder of about 300 mesh coated with HDEHP (2,2 diethyl-hexyl-orthophosphoric activator). The Sr leachate from the chromatographic separation was evaporated to dryness and loaded onto a single Ta filament with 1 drop H_2PO_4 and 1 drop HNO_3. Rb was similarly loaded onto a side filament of Ta with a central Ta filament, whereas Sm and Nd were loaded onto a side filament of Ta with a centre filament of Re. Sr, Sm and Nd were determined by thermal ionisation solid-source on a VG354 multi-collector instrument using Pyramid TIMS software, and Rb on a MM30 solid-source mass spectrometer. Sr-isotopic data were normalized to $^{86}Sr/^{88}Sr$ = 0.1194. Runs of SRM-987 $SrCO_3$ standard yielded an $^{87}Sr/^{86}Sr$ ratio of 0.71023±20 (2σ). Nd-isotopic data were normalized to $^{146}Nd/^{144}Nd$ = 0.7219. The mean of the measured $^{143}Nd/^{144}Nd$ ratio of an internal standard (Goodfellow Nd metal) was 0.51125±15 (2σ). Total procedural blanks were less than 1 ng for Sr, <500pg for Sr and 0.25 ng for Sm and Nd.

ISOTOPIC RESULTS

A detailed Rb/Sr and Sm/Nd study of fluorite from a range of settings in the granites of the Bushveld Complex was undertaken to determine the initial ratio of the fluorite and hence of the granites themselves and to evaluate the evolution of the secondary fluids.

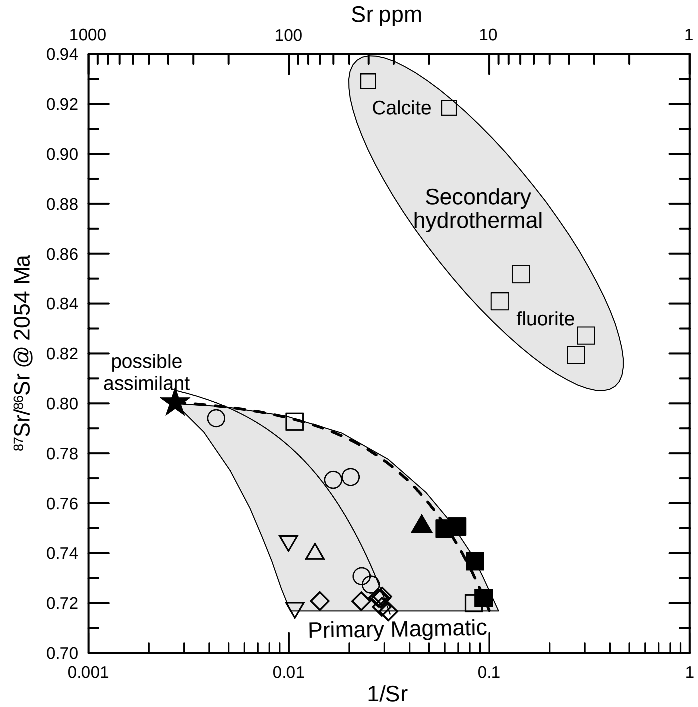
Rb-Sr and initial $^{87}Sr/^{86}Sr$ variations in fluorite

The $^{87}Sr/^{86}Sr$ initial ratios were corrected to 2054 Ma as the disseminated fluorite and most pipes and veins are believed to have formed at the late-stage of Bushveld granite crystallisation. The Rb content of all fluorite samples is very low (only one sample above 1.5 ppm). Since fluorite has a low Rb/Sr ratio, the back correction of the $^{87}Sr/^{86}Sr$ value has minimum uncertainty so the initial $^{87}Sr/^{86}Sr$ of the fluid from which it crystallised can be determined. Rb-Sr isotopic data for fluorite and two samples of calcite, and calculations of the R_o values are given in Table 2, divided according to the style of fluorite mineralisation. At some localities (e.g., Zaaiplaats), more than one type of mineralisation may be present. The samples from the Vergenoeg pipe represent the simplest data set. These fluorites have low Sr concentrations (32 to 70 ppm), and R_o in the range 0.7166 to 0.7226 with the lowest initial ratio at 2054 Ma of 0.71664 given by a disseminated fluorite from a fayalite-magnetite assemblage in a core from 472 m depth in the pipe. On a plot of $^{87}Sr/^{86}Sr$ vs 1/Sr ppm (Fig. 11a), the Vergenoeg samples are closely clustered. Fluorites from Buffalo show a wide range of both Sr content (from 39 to 231 ppm) and R_o, (0.7274 to 0.7949), the lower values of which approach those observed at Vergenoeg. There is a weak positive correlation between Sr

Table 2 : Rubidium-stontium isotope data for fluorite and calcite samples

No	locality	Rb ppm	Sr ppm	^{87}Rb	^{86}Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	±	2 se	$R_{initial}$ @ 2054	±	2 sigma
					disseminations in reddened roof facies							
SP3	Spoedwel	1.43	74.13	0.40	7.14	0.05561	0.742514	±	30	0.740868	±	0.0002
GC3969	Zaaiplaats	0.59	11.80	0.17	1.14	0.14360	0.740948	±	134	0.736698	±	0.0002
GC1723	Zaaiplaats	0.58	16.70	0.16	1.61	0.09983	0.752767	±	51	0.749812	±	0.0002
TM2	Zaaiplaats	0.68	10.68	0.19	1.03	0.18478	0.727556	±	34	0.722087	±	0.0002
					pegmatitic pods							
LR1	Zaaiplaats	0.22	6.96	0.06	0.66	0.01088	0.852091	±	76	0.851769	±	0.0002
LR2	Zaaiplaats	0.05	11.95	0.01	1.15	0.01088	0.720257	±	65	0.719935	±	0.0001
LR3	Zaaiplaats	0.16	93.54	0.05	8.97	0.00499	0.792833	±	59	0.792685	±	0.0002
LR4	Zaaiplaats	0.28	14.45	0.08	1.39	0.05658	0.752335	±	60	0.750661	±	0.0002
TM1	Zaaiplaats	0.21	8.87	0.06	0.85	0.06779	0.842905	±	52	0.840899	±	0.0002
TM3	Zaaiplaats	0.09	3.70	0.03	0.35	0.07045	0.821466	±	89	0.819381	±	0.0002
TM4	Zaaiplaats	0.10	3.29	0.03	0.32	0.08847	0.829818	±	290	0.827200	±	0.0002
					stockworks in felsic volcanics							
GC1673	Zwartkloof	0.09	93.37	0.03	9.02	0.00290	0.717059	±	22	0.716973	±	0.0001
GC1808	Zwartkloof	0.64	100.41	0.18	9.68	0.01834	0.744348	±	25	0.743805	±	0.0002
					stockworks in metasedimentary xenoliths in granite							
GC1670	Buffalo	2.36	39.01	0.67	3.76	0.17497	0.732571	±	18	0.727393	±	0.0002
Buf06	Buffalo	0.45	230.73	0.13	22.12	0.00572	0.794229	±	44	0.794060	±	0.0002
Buf07	Buffalo	0.28	43.34	0.08	4.18	0.01859	0.731319	±	68	0.730769	±	0.0002
Buf 08C	Buffalo	0.14	60.15	0.04	5.78	0.00691	0.76958	±	26	0.769376	±	0.0002
Buf08PP	Buffalo	0.63	49.23	0.18	4.73	0.03699	0.7716	±	47	0.770505	±	0.0002
					pipe cross-cutting the volcanic pile							
Verg06	Vergenoeg	0.07	34.37	0.02	3.32	0.00607	0.718698	±	45	0.718518	±	0.0001
Verg07	Vergenoeg	0.47	34.87	0.13	3.37	0.03916	0.72293	±	17	0.721771	±	0.0002
Verg08P	Vergenoeg	0.20	70.13	0.06	6.77	0.00815	0.721037	±	24	0.720796	±	0.0001
Verg08W	Vergenoeg	0.11	43.57	0.03	4.21	0.00709	0.720962	±	71	0.720752	±	0.0001
Verg11	Vergenoeg	0.78	35.86	0.22	3.46	0.06235	0.723942	±	28	0.722097	±	0.0002
Ver38/440	Vergenoeg	0.66	34.24	0.19	3.31	0.05555	0.724233	±	16	0.722589	±	0.0002
Ver124/472	Vergenoeg	0.81	31.92	0.23	3.08	0.07312	0.718802	±	27	0.716638	±	0.0002
					pipe cross-cutting granite							
HBL21	Houtenbek	1.24	21.72	0.35	2.09	0.16501	0.756705	±	65	0.751821	±	0.0002
					late calcite							
TM5	Zaaiplaats	0.84	15.89	0.24	1.50	0.15614	0.923069	±	244	0.918448	±	0.0002
TM6	Zaaiplaats	0.10	40.07	0.03	3.79	0.00717	0.929561	±	30	0.929349	±	0.0002

A



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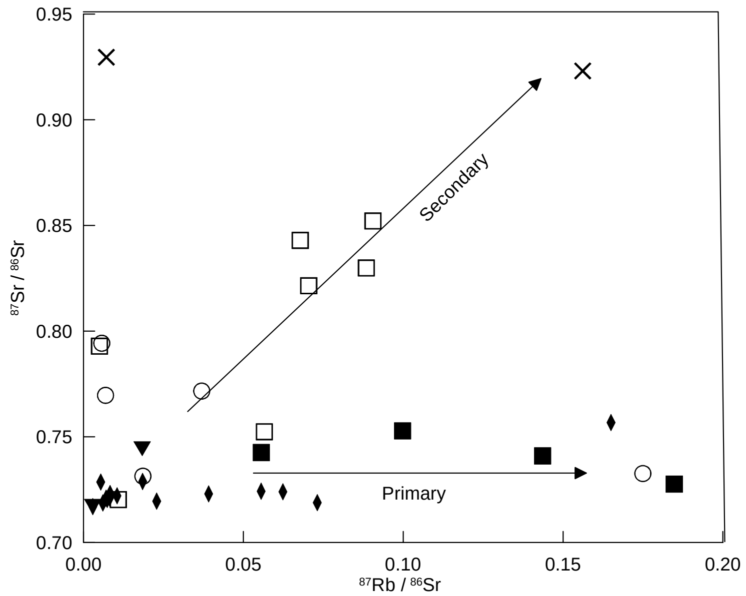

Figure 11. *(a) Plot of Sr versus the Initial ratio. Symbols are Zaaiplaats primary fluorite (closed squares), Zaaiplaats secondary fluorite (open squares), Buffalo (circles), Vergenoeg (diamonds), Spoedwel (up triangle), Zwartkloof (down triangles) and Houtenbek (filled triangle). The linear fits are dashed line for Zaaiplaats and solid line for Buffalo. The data form two distinct fields: the primary field showing a mixing relationship in the case of Buffalo and Zaaiplaats (possibly also for Zwartkloof and Spoedwel) between a primary magmatic signature, with an initial ratio of between 0.7166 (Vergenoeg) and a Sr concentration (in fluorite) of between c. 10 and 100 ppm, and another component with a ratio of c. 0.80 and a Sr concentration (in fluorite) of c. 370 ppm. This latter component could be derived from Rb-rich enclosing felsite (Zaaiplaats) and sediments (Buffalo), which are up to 10 Ma older than the intruding granites, or from within the granite mass itself as a late magmatic phase, provided a high enough Rb/Sr ratio can be achieved. (b)* $^{87}Rb/^{86}Sr$ *vs* $^{87}Sr/^{86}Sr$ *showing primary and secondary fluorite.*

content and R_o in the Buffalo data set (Fig. 11a). The two samples from Zwartkloof and the single sample from Spoedwel fall along a parallel trend to those from Buffalo. In contrast, the data from Zaaiplaats fall into two separate groups (Fig. 11a). The first group, which are regarded as primary, define a trend parallel to the previous trend, but at lower Sr (11-17 ppm) and slightly higher R_o (0.7220 – 0.7498). The single sample from Houtenbek falls along this trend. In contrast, the second group regarded as secondary (including some of the pegmatitic fluorite), has even lower Sr (as low as 3 ppm) and much higher R_o (>0.80). Two groups of data are also apparent on Figure 11b.

For Vergenoeg there is a limited range of $^{87}Sr/^{86}Sr$, but a spread of variable, but low $^{87}Rb/^{86}Sr$ ratios, whereas for the pegmatitic fluorite from Zaaiplaats, the $^{87}Sr/^{86}Sr$ initial ratio ranges to >0.85, also with variable but low $^{87}Rb/^{86}Sr$ ratios. Furthermore, one colour-zoned fluorite pod from Zaaiplaats shows an extreme variation of data. The pod, which is 10 cm in diameter (Fig. 12), comprises a core of light- to dark- green fluorite, enclosed in purple fluorite with a discontinuous rim of colourless fluorite within reddened granite. There is a variation in $^{87}Sr/^{86}Sr$ from 0.7199 for the dark-green core to 0.8517, for the purple zone. In addition, two samples of late calcite adjacent to coarse fluorite in the same pegmatite pod have extremely high R_o values of over 0.9 (Fig. 11b).

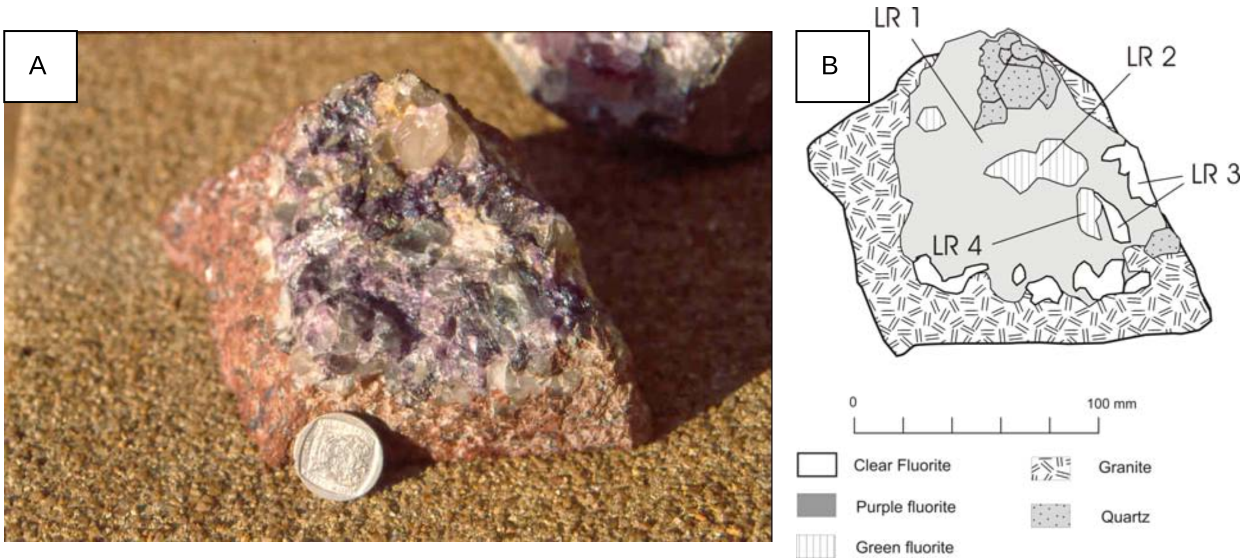

Figure 12. ***(a) Photograph of zoned pegmatitic fluorite pod, in Bobbejaankop granite, Zaaiplaats. (b) Sketch of the pegmatitic pod showing colour variations and location of samples.***

Rb-Sr and initial $^{87}Sr/^{86}Sr$ variations for granite minerals

The authors also attempted to determine the Sr initial ratios for minerals from a 'primitive' granite dyke at the time of emplacement and for an 'evolved' feldspar from the Zaaiplaats Granite. The data for the granite minerals are shown in Table 3. Perthite samples from the Steelpoort Granite vein show a negative correlation in Rb and Sr contents (155-408 ppm and 45-70 ppm, respectively). However, the R_o values range from 0.805 for the sample with the lowest Sr content, to progressively lower and impossible values of less than 0.7 with increasing Sr content. The single plagioclase composition contains 164 ppm Rb and 118 ppm Sr (Table 3). Because the partition coefficients for Rb and Sr between and magma and plagioclase are in the order of 0.1 and 3, such concentrations in the plagioclase appear anomalous. The chloritised mica also has atypical values in only containing <10 ppm Rb, and one sample having 72 ppm Sr.

Table 3. Sm-Nd isotope data for selected fluorite samples. Data for samples with an asterisk are not plotted in Figs 13 or 14 either because of high errors or because of low initial ratios, but are included as comparative data to similar samples

Sample no	Locality	Sm ppm	Nd ppm	^{147}Sm	^{144}Nd	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	±2se	Ro@ 2054
				Fluorite disseminated in granites, in pipes and stockworks					
GC1723	Zaaiplaats	34.27	100.90	5.0334	24.0100	0.20536	0.51298	±21	0.51020
TM2	Zaaiplaats	49.79	130.07	7.3124	30.9500	0.23144	0.51363	±17	0.51050
GC1673	Zwartkloof	80.51	228.87	11.8256	54.4600	0.21271	0.51302	±21	0.51014
GC1808	Zwartkloof	63.58	173.78	9.3390	41.3500	0.22124	0.51341	±20	0.51042
GC1670	Buffalo	62.63	285.44	9.1986	67.9200	0.13267	0.51211	±14	0.51031
Buf07	Buffalo*	66.48	296.71	10.1367	56.6795	0.17519	0.51225	±17	0.50988
Verg07	Vergenoeg	55.67	228.20	8.1760	54.3000	0.14750	0.51195	±67	0.50996
HBL21	Houtenbek	23.64	107.92	3.4723	25.6800	0.13245	0.51196	±34	0.51017
				Fluorite in veins and pegmatitic pods					
Buf08PP	Buffalo	3.38	5.59	0.5137	1.3305	0.37822	0.51193	±19	0.50682
LR1	Zaaiplaats*	0.33	1.03	0.0491	0.2319	0.20741	0.51147	±131	0.49896
LR2	Zaaiplaats*	31.00	79.28	4.5528	18.8000	0.23723	0.50917	±39	0.50650
LR3	Zaaiplaats	0.58	1.22	0.0845	0.2900	0.28543	0.51423	±39	0.51037
LR4	Zaaiplaats	30.97	69.59	4.5492	16.5600	0.26910	0.51361	±20	0.50997
TM1	Zaaiplaats	0.85	2.06	0.1246	0.4900	0.24910	0.51275	±16	0.51244
TM3	Zaaiplaats*	0.18	0.66	0.0264	0.1600	0.16163	0.51267	±948	0.51048
TM4	Zaaiplaats	0.17	1.36	0.0248	0.3225	0.07533	0.51162	±18	0.50626

Sm-Nd variations in fluorite

A smaller set of fluorite samples was analysed for Sm-Nd compared to those analysed for Rb-Sr (Table 4). Vergenoeg fluorite has high contents of Sm and Nd (56 and 228 ppm, respectively) whilst other samples of primary fluorites from pipes and stockworks (Buffalo, Zwartkloof, Houtenbek and Zaaiplaats) have similar or decreasing abundances in Sm and Nd to 23 and 108 ppm, respectively. In contrast, the pegmatitic fluorites from Zaaiplaats that displayed very high R_o values together with a late fluorite from Buffalo, have low abundances of Sm and Nd (to 0.1 and 1ppm, respectively - Table 3). Samples from the colour-zoned fluorite pod from Zaaiplaats show two groups of data. For the green core (samples LR1 and LR2) Sm and Nd content is similar to some primary fluorite (31ppm Sm and Nd *c.*70 ppm), whereas the outer purple and colourless zones have low abundances of Sm and Nd (to 0.1 and 1ppm respectively) consistent with other pegmatitic fluorite.

Therefore, as with the Sr data, two groups of data emerge on plots of Nd against other elements and ratios (Figs. 13a-d), one for primary disseminated fluorite with Nd >100 ppm, Sm >10 ppm, low Rb/Sr, and low R_o , and one for secondary pegmatitic or vein-hosted fluorite with Nd <10 ppm, Sm generally <1 ppm and high R_o. Data for $^{147}Sm/^{144}Nd$ vs $^{143}Nd/^{144}Nd$ are shown in Figure 14 and the initial $^{143}Nd/^{144}Nd$ for all samples are shown as a histogram on the y axis.

Although Sm and Nd are incompatible light REE’s that increase in concentration with increasing degrees of differentiation, Nd is usually concentrated in the fluid phase relative to Sm so that the Sm/Nd ratio decreases during the course of vapour-saturated fractional crystallisation (Bai and Van Groos, 1999). However, Sm/Nd ratios in analysed samples are low for most samples, and do not systematically increase in samples associated with cassiterite mineralisation at Zaaiplaats.

Table 4 : Mineral data for granite sample. G18 is microperthite from Zaaiplaats granite, the other minerals are from the granite dykes near Steelpoort

Sample	mineral	Rb ppm	Sr ppm	^{87}Rb	^{86}Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	2se	Ri@2054
K24	perthite	154.93	45.61	43.66	4.25	10.164	1.106710 ±	247	0.805340
K85	perthite	363.19	69.52	102.33	6.46	15.670	1.130551 ±	98	0.666787
K86	perthite	408.49	65.62	115.10	6.08	18.707	1.149955 ±	44	0.596311
K87	chlorit. biotite	7.75	7.11	2.18	0.68	3.164	0.783845 ±	261	0.690198
K88	chlorit. biotite	9.41	72.22	2.65	6.98	0.376	0.719430 ±	142	0.708309
L26	perthite	437.03	62.89	123.14	5.78	21.058	1.124099 ±	106	0.617748
L27	plagioclase	164.04	118.48	46.22	11.34	4.031	0.817987 ±	50	0.698685
G18	perthite	581.53	11.71	163.86	0.81	199.94	4.772590 ±	145	-1.1624

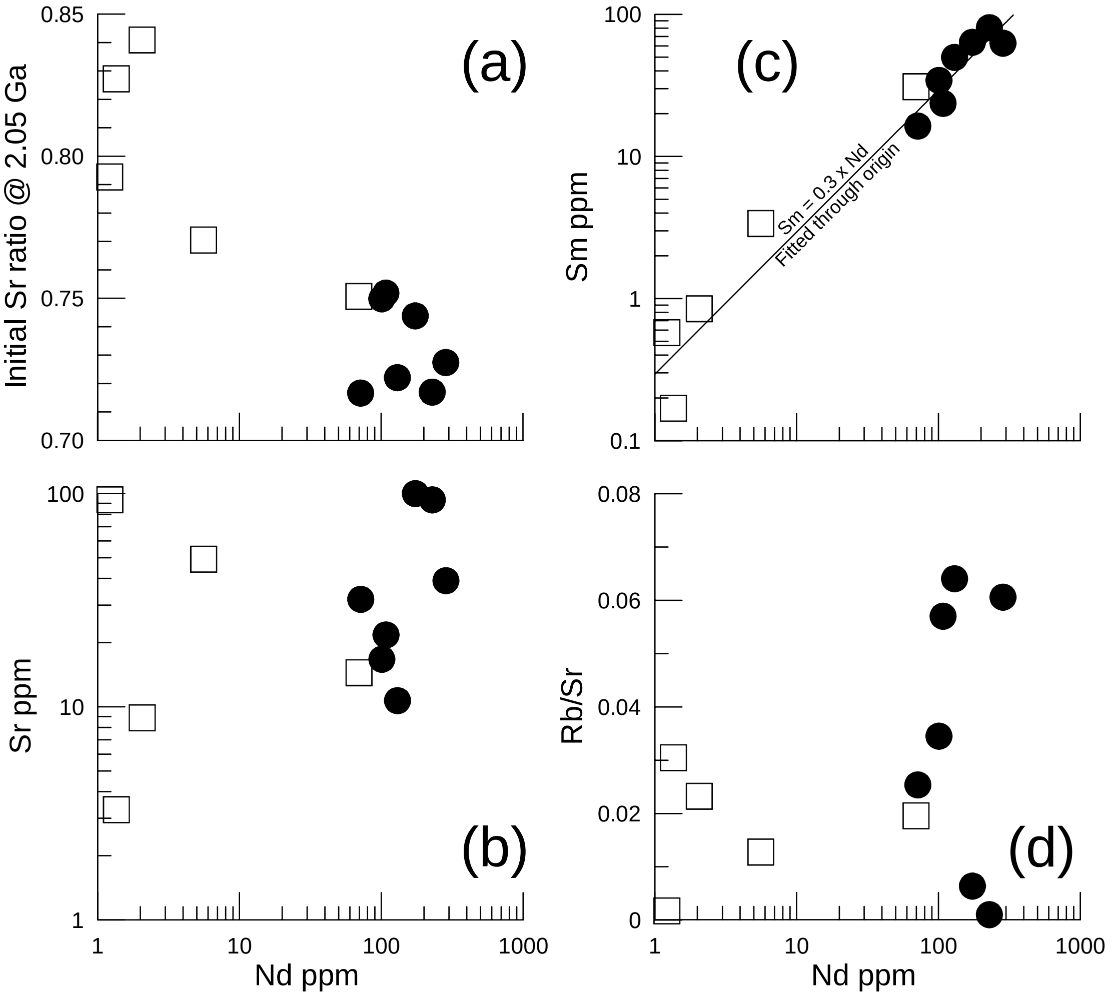

Figure 13. *Nd ppm plotted against (a) $^{87}Sr/^{86}Sr$ ratios (b) Sr ppm (c) Sm ppm and (d) Rb/Sr. Circles are primary fluorites, and squares are pegmatitic fluorites. The green core of a zoned fluorite pegmatite pod (LR4) plots with primary fluorites and is interpreted as representing an original late magmatic fluorite rimmed by later secondary fluorite.*

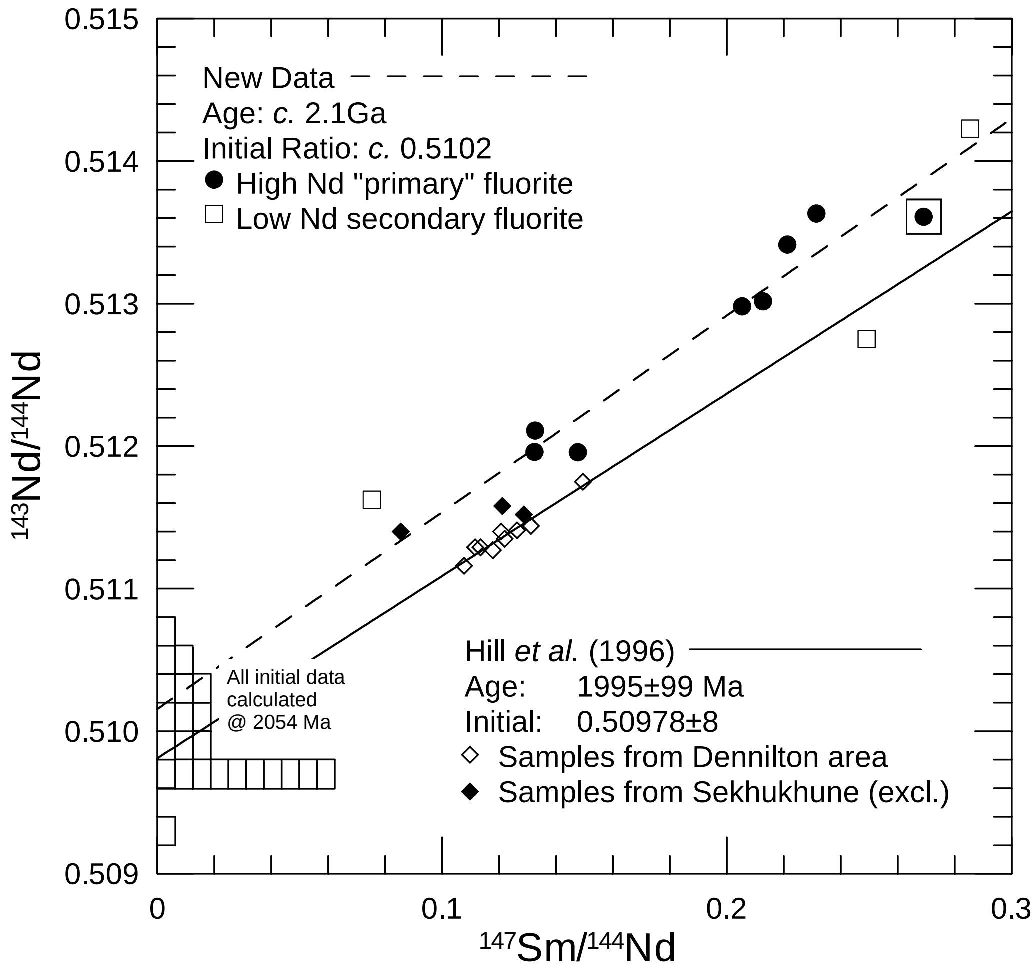

Figure 14. *$^{143}Nd/^{144}Nd$ ratios plotted against $^{147}Sm/^{144}Nd$. Data from the primary fluorites approximate to an isochron c. 2100 Ma (dotted line), whilst the data from granites analysed by Hill et al.(1996) (excluding those from Sekhukhune) fit on an isochron with a lower $^{143}Nd/^{144}Nd$ initial ratio with an age of 1995 ± 99 Ma (solid line). All the calculated initial ratios are shown as a histogram on the y axis. LR4 is shown as a dot within an open square as it has both primary and secondary characteristics.*

DISCUSSION

Granite isotopic data

Previously reported initial $^{87}Sr/^{86}Sr$ ratios from whole-rock Bushveld granites are variable and range from 0.715-0.729 (Davies *et al.*, 1970), 0.715 ± 0.009 (Hunter and Hamilton, 1978) 0.724 ± 0.016 (Robb *et al.*, 1994) and 0.7994 ± 0.003 (Hill *et al.*, 1996). Such elevated $^{87}Sr/^{86}Sr$ ratios in Bushveld granites have been variously attributed to:

(1) late-stage mineral assemblages with anomalously high and variable initial ratios resulting from gaining ^{87}Sr lost from biotite and/or feldspar, during prolonged rock-fluid interaction (Walraven, 1981; Hill *et al.*, 1996); or

(2) enhancement of ^{87}Sr growth by ^{87}Rb decay in high Rb/Sr residual melts during a long magmatic crystallisation period (McCarthy and Cawthorn, 1980).

The R_o obtained on mineral separates from the granite dykes near Steelpoort show that the isotopic ratios and concentrations have been 'disturbed'. Thin sections indicate that feldspars and biotites in the granite have been slightly sericitised and chloritised. Plotted isotopic and $^{87}Rb/^{86}Sr$ compositions of chloritised mica are extremely low compared to the expected values in pristine mica. Isotopic data on these phases (Table 3) show that the biotite has lost almost all its primary Rb (*c*. 8 ppm compared to an expected >500ppm) and has gained Sr (< 72 ppm compared to an expected <10 ppm). $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ compositions of this chloritised mica are extremely low compared to the expected values in pristine mica ($^{87}Rb/^{86}Sr$ *c.* 100-1000) and has impossible initial ratios for 2054 Ma. Thus minor alteration had a significant effect on the Sr isotopes. The present-day $^{87}Sr/^{86}Sr$ value of 0.719 on sample K88 confirms that the alteration in the granite vein occurred very early, since a fresh biotite ($^{87}Rb/^{86}Sr$ >100) would be expected to have developed a very high $^{87}Sr/^{86}Sr$ (>>0.7194) within 10 Ma after formation. Chlorite does not reflect this high value and so it is suggested that the biotite was stripped of its Rb during chloritisation by an "autometasomatic" or "late magmatic" process. The gabbronorite surrounding the granite dykes is still fresh and unaltered, consistent with the suggestion that alteration in the granite was related to fluid activity generated within the granite dyke at the time of emplacement, and was not a much later overprint. Since the Sr and Rb contents of the plagioclase and perthite in the granite samples analysed have been drastically re-set, we conclude that none of the major minerals in any granite sample is likely to give reliable information on initial $^{87}Sr/^{86}Sr$ values and hence the importance of the data available from the fluorite.

FLUORITE ISOTOPIC DATA

The Zaaiplaats granite has high Rb and low Sr in comparison with other Bushveld granites and the primary fluorite disseminated in this granite and within pegmatitic pods have low Rb (generally <<1ppm) and low Sr (10.68 - 16.70 ppm). This observation is in contrast to some other evolved high Rb, low Sr granites (e.g., Davis Lake monzogranite, Nova Scotia) where fluorites are reported with up to 13 ppm Rb and 1420 ppm Sr and with variable initial $^{87}Sr/^{86}Sr$ ratios of 0.7132-0.77495 (Richardson *et al.,* 1990). The absolute abundances of Rb and Sr in fluorite cannot accurately be related to the composition of the granite magma from which it is assumed they formed. The reason is that the fluorite presumably formed from a fluid, and the partition coefficients between fluorite and fluid are not known. The fluid segregated from a granitic melt at a stage when the Sr content was quite low and the partition coefficient for which between fluid and melt is quite low. Hence absolute values for Sr in fluorite are quite difficult to interpret, but relative changes will provide information on the stage of evolution of the fluids from which various fluorite assemblages formed. Rb contents in fluorite are all extremely low (less than 2ppm) which probably reflects the low partition coefficient between fluorite and fluid. Sr values are highly variable, ranging from 3 to 94 ppm (and one extreme value of 231 ppm). The range in R_o values is also large from 0.716 to 0.851. The variation displayed by these two parameters is shown in Figures 11a and b.

The deposit that shows the least variability is Vergenoeg (Table 2) with Sr from 32-70 ppm, and R_o from 0.7166-0.722. Since there are seven analyses varying from surface to 472 m depth, it suggests that the Vergenoeg pipe formed from a single event from a well-homogenised source. There are two proposed hypotheses for the origin of this deposit: (1) an immiscible iron-rich liquid (Crocker, 1985) or, (2) a separate vapour phase (Borrok *et al.*, 1998). However, in both cases it is envisaged as being derived from the underlying granite magma. For the present purposes, the process of origin is less important than the fact that is was derived from Bushveld granite magma. That being the case, we conclude that the granitic magma had a R_o value of about 0.72.

All other deposits show a range of R_o values and suggest that multiple sources were involved and that the system was not homogenised prior to the formation of the different fluorite generations. In terms of the data presented in Table 2, the next simplest deposit is Buffalo. Two samples have Sr and R_o values comparable to the average for Vergenoeg, which implies that those two samples were generated from a similar source. The three other samples display a regular relationship of increasing Sr and R_o that may be consistent with mixing between two end-members. The one end-member we identify as granite. The host to the fluorite veins are large metasedimentary rafts, inferred to be derived from the Transvaal Supergroup. Analyses by Watson and Snyman (1975) have shown that these metasediments contain more Ca than granite. They do not present data for Sr contents, but the higher Ca indicates that they may also have higher Sr. We suggest that these metasedimentary rocks provided the second component, possibly by reaction with the fluid producing the fluorite, with up to 250 ppm Sr and R_o of 0.8 depending on the extent of rock-fluid interaction.

The data for Zwartkloof may be interpreted in a similar way. One sample yields a low R_o value of 0.717 and Sr content close to the highest value identified for Vergenoeg. The other sample has slightly higher Sr and much higher R_o. The deposit is hosted by Rooiberg felsites that need not have the same Sr and R_o values as the metasedimentary material at Buffalo, but a mixing line can be constructed to the same contaminant, although two points do not constrain the trend rigorously. The single data point for Houtenbek can be interpreted using the same principles. It contains less Sr than those previously discussed and it is possibly significant that the fragments in the breccia include metasedimentary xenoliths, possibly analogous to Buffalo. We would suggest that the fluorite from this locality formed by a mixing of a more evolved fluid derived from granite (and hence lower in Sr) with a component from the metasedimentary xenoliths. Support for the existence of a more evolved, lower Sr fluid derived from the granite body can be found by examination of the Zaaiplaats data. The sample with the lowest R_o value of 0.720, and hence derived totally from the granitic fluid, has 12 ppm Sr. Other samples of the disseminated mineralisation define a mixing trend with a second component possibly similar to that envisaged for the other deposits.

There is a second suite of samples from Zaaiplaats that are chemically very different from those just described. Four of the samples taken from the pegmatitic pods contain slightly lower Sr and higher Ro values than the previous set (Table 2). Two other samples (LR2 and LR4) occur as cores to a pegmatitic pod (Fig. 4). They have values that group them with the first generation of fluorite (higher Sr and lower R_o), but they are overgrown by a later generation of different-coloured fluorite that defines the second group. Calcite occurs associated with the pegmatitic fluorite. It has higher Sr content and R_o values than fluorite. The higher Sr content may not have any significance, since it is not known what the partition coefficients are for Sr between calcite and fluid, and fluorite and fluid. The higher Sr values in calcite than fluorite may indicate that the former is much larger than the latter.

The two distinct groupings of samples indicate different processes of genesis. We suggest that the simplest data set from Vergenoeg indicates a single stage magmatic source from a granitic parent. The other samples, except some pegmatite samples from Zaaiplaats, indicate mixing between variably evolved fluids derived from this granite and a variety of roof rocks, mainly metasedimentary rocks and felsites. We refer to this group of fluorites as the magmatic phase. The second group we suggest, on textural grounds (since they occur in pegmatites), reflect a hydrothermal stage of mineralisation.

The low R_o ratios and elevated Sm and Nd contents are consistent with a magmatic origin for the primary fluorite in granites and volcanic pipes (e.g., Vergenoeg). Fluid inclusion studies from Vergenoeg and Zaaiplaats also suggest that the earliest fluorite is magmatic in origin. According to Borrok *et al*. (1998), fluorite at Vergenoeg formed from fluids of late magmatic origin at >500°C, >67 eq. wt% NaCl, with later phases from fluids between 500 and 150°C at 1-35 eq. wt% NaCl. Stable oxygen isotope analyses of early fayalite and Ti-magnetite yielded calculated water compositions for these temperatures that are typical of magmatic water ($\partial^{18}O$ = 7-8‰ at 500°C). Similarly, a fluid inclusion study of Zaaiplaats by Pollard *et al*. (1991) showed that early fluid inclusions in samples from a pipe in the Bobbejaankop Granite have homogenisation temperatures <600ºC with a salinity of 68 wt% eq. NaCl evolving to lower temperatures and salinity (15 eq. wt% NaCl) during vein and cavity fill. The $\partial^{18}O$ for granite whole rocks ranges from +9.2 to +9.9‰. Modelling indicated interaction between granites and a magmatic fluid with final isotopic exchange below 400ºC.

The distinction between the magmatic and hydrothermal phases of fluorite formation using Sm and Nd abundances is even greater than for Sr. Fluorite formed at the magmatic stage has 20-80 ppm Sm and 100-300 ppm Nd, whereas those formed during the hydrothermal phase have less than 3 ppm Sm and 5 ppm Nd. The sample LR4, from the core of a zoned pegmatitic fluorite, which had a magmatic signature in terms of Sr and R_o , displays the same relationship in terms of Sm and Nd, and so its affiliation to the magmatic group appears to be confirmed.

For the primary fluorite, most samples fall on an array indicating an age of *c*. 2050 Ma (shown as 2.1 Ga on Fig. 14), but with a large scatter. The initial ratio also has a large error, but does indicate a similar value and scatter to data from the Sekhukune plateau of Hill *et al*. (1996), but is higher than their value for the Dennilton area that indicates an age of 1995 ± 99 Ma and initial $^{143}Nd/^{144}Nd$ of 0.50978 ± 8, but these observations are only partly quantifiable. For the secondary fluorite, the measured $^{143}Nd/^{144}Nd$ is similar to that of the early fluorite. The scatter evident in the fluorite and also in the data of Hill *et al.* (1996) is due to the wide geographic, petrological and geochemical spread, and the influence of assimilation and secondary processes.

Data for the secondary fluorite and calcite at Zaaiplaats are distinct. Either this later fluorite-calcite assemblage was related to migration of fluids that evolved from the saline magmatic fluids to lower temperatures and salinity during vein and cavity fill (Pollard *et al.*, 1991), with variable contamination of primary magmatic fluids by radiogenic country rock, or they were related to a later hydrothermal episode that occurred 70-100 Ma after magma emplacement at *c.* 2054 Ma.

The rare earth element concentrations are orders of magnitude lower in the secondary fluorite than those in the primary magmatic fluorites and it is unlikely to be simply an evolution from a magmatic to a hydrothermal fluid. Further, Robb *et al.* (2000) modelled associated heat flow for the Lebowa Granite Suite based on the assumption that the granites were emplaced 250 000 years after the intrusion of the 7 km-thick Rustenburg Layered Suite. These authors included a significant radiothermal heat producing capacity for the granite of 30μWm^{-3} and considered that at the time of granite emplacement the underlying Rustenburg Layered Suite was still a major thermal anomaly in the crust that kept the base of the granite sheet above its solidus temperature for some time. They calculated that 4 Ma after emplacement, the granite and surrounding crust had cooled to around 200°C and that hydrothermal circulation would have effectively ceased. Hence any hydrothermal activity in the Bushveld Complex that significantly postdates *c.* 2050 Ma must have been externally derived. A U-Pb age of 2049 ± 5 Ma for a late magmatic cassiterite from Rooiberg (R.A.

Armstrong; in prep.) is consistent with the granite emplacement age. Isotopic and $^{87}Rb/^{86}Sr$ compositions of the plagioclase, perthite, and the chloritised mica from the granite vein plot on a growth curve of the bulk of the granite samples indicating an age of *c.* 2000 Ma (Fig. 15). However, the $^{87}Rb/^{86}Sr$ values of chloritised mica are extremely low compared to the expected values in pristine mica, which should be greater than 100. The curves in Figure 15 indicate evolution of minerals with $^{87}Rb/^{86}Sr$ up to 1000 at 10 million year intervals, beginning at *c.* 2054 Ma. This indicates that the micas would have attained their *present day* ratios <10 million years after crystallisation and thus the chloritisation event, which reduced the $^{87}Rb/^{86}Sr$ to <5, occurred within this time. The data reported from the Bobbejaankop Granite at Zaaiplaats (Walraven *et al*., 1990b) are clearly disturbed and scattered with a wide range of spurious model ages that give an average slope and age of *c.* 1500 Ma. The evolution of this bulk average for the granites (assuming only ^{87}Sr loss) is shown by the vertical arrow, which indicates that, in general, the rocks of the Zaaiplaats area evolved very high $^{87}Sr/^{86}Sr$ ratios very rapidly. This is particularly so for any biotite which is expected to have $^{87}Sr/^{86}Sr$ significantly greater than whole rocks or any feldspar. This hypothesis is supported by the data for the pale fluorite and calcite which record the $^{87}Sr/^{86}Sr$ composition of the fluids circulating in the rocks at the time of their precipitation. These compositions could not have been generated from the average bulk rocks later (or much earlier) than *c*. 70-100 Ma after crystallisation as indicated by the intersections of the vertical arrow.

The isotopic data (and age data of Robb *et al*., 2000) indicate that these secondary fluorites are therefore related to a much later thermal event that occurred 70-100 Ma after intrusion, during which time lower salinity fluids migrated through the rocks. These are not directly related to the magmatic event of *c.* 2054 Ma as suggested by Pollard *et al.* (1991). The wide scatter of $^{87}Sr/^{86}Sr$ data in the granites at Zaaiplaats, due to alteration, open system behaviour, surficial processes, and apparent very young ages shown by the feldspars, are not recorded in primary magmatic fluorite from Zaaiplaats or the feldspar and chlorite from the Steelpoort granite veins, which record the primary magmatic event.

A number of independent lines of evidence indicate that there were significant hydrothermal events around 2000 Ma over the whole of the northern Kaapvaal Craton. Mica model ages from the Bushveld Magmatic Province indicate significant resetting at *c*. 2025 Ma (Coetzee, 1995). There was significant transpressive deformation in the Limpopo Belt immediately to the north of the Bushveld Complex at *c.* 2000 Ma (Kamber *et al*., 1995; Holzer *et al*., 1998). Robb *et al.* (2000) give a U-Pb SHRIMP age of 1957 ± 15 Ma for a hydrothermal zircon from Spoedwel in the Bushveld granites, and Xenophontos *et al*. (2001) recorded a model lead age of 1957 ± 110 Ma on a late pyrite generation in the Witwatersrand Basin. All these ages suggest a later event capable of re-setting mineral ages and generating a hydrothermal system.

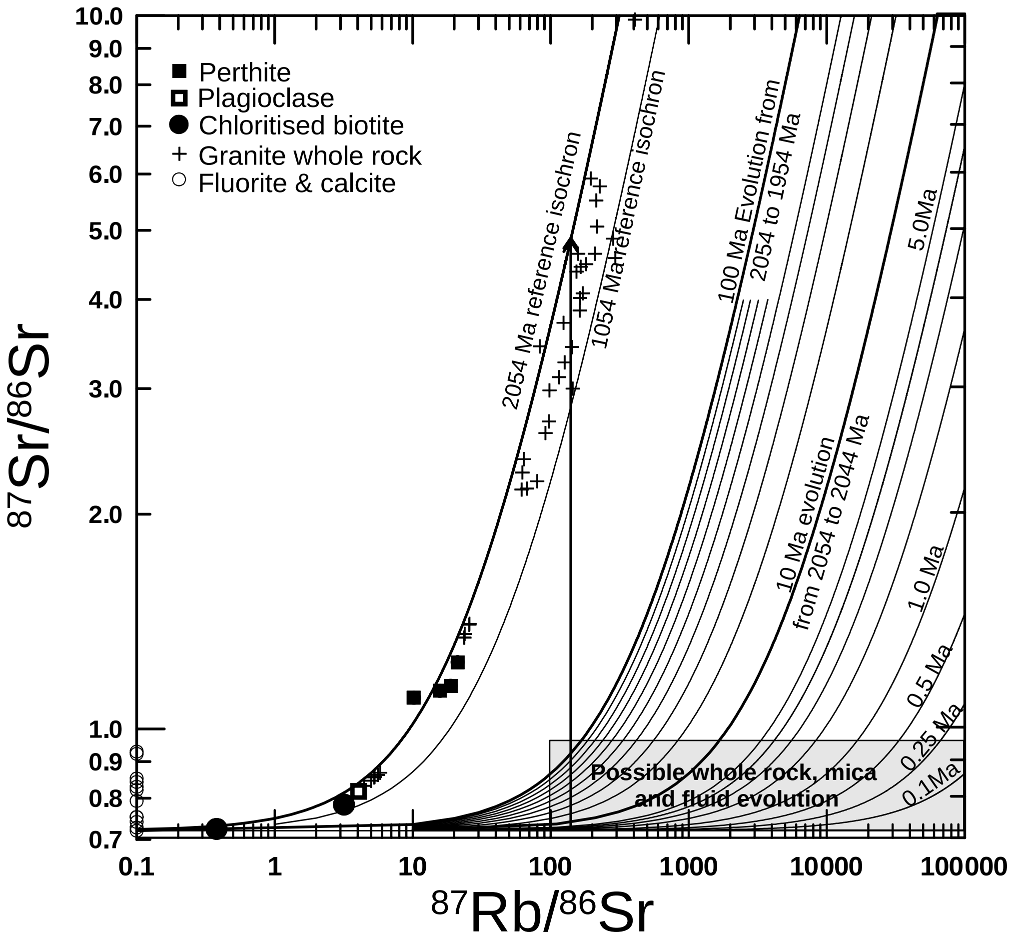

Figure 15. *Rb/Sr isotopic compositions and evolution of minerals and rocks from the Bobbejaankop Granite at Zaaiplaats (Walraven et al., 1990b), and data on a granite vein near Steelpoort and the fluorite and calcite reported on here. Isotopic and $^{87}Rb/^{86}Sr$ compositions of the plagioclase, perthite and the chloritised mica from the granite vein plot on a growth curve of the bulk of the granite samples indicating an age of c. 2000 Ma. However, the $^{87}Rb/^{86}Sr$ chloritised mica are extremely low compared to the expected values in pristine mica, which should be greater than 100. The curves indicate evolution of minerals with $^{87}Rb/^{86}Sr$ up to 1000 at 10 million year intervals, beginning at 2054 Ma. This indicates that the micas would have attained their present day ratios <10 million years after crystallisation and thus the chloritisation event which reduced the $^{87}Rb/^{86}Sr$ to <5 occurred within this time.*

The data reported from the Bobbejaankop Granite at Zaaiplaats (Walraven et al., 1990b) are clearly disturbed and scattered with a wide range of possible, but spurious model ages.The average slope and age calculated for the Zaaiplaats data is shown (c.1500 Ma). The evolution of this bulk average for the granites (assuming only ^{87}Sr loss) is shown by the vertical arrow, which indicates that, in general, the rocks of the Zaaiplaats area evolved very high $^{87}Sr/^{86}Sr$ ratios very rapidly. This is particularly so for any biotite, which is expected to have $^{87}Sr/^{86}Sr$ significantly greater than whole rocks or any feldspar. This is also illustrated by the pale fluorite and calcite, which record the $^{87}Sr/^{86}Sr$ composition of the fluids circulating in the rocks at the time of their precipitation. These compositions could not have been generated from the average bulk rocks later than c. 70-100 Ma after crystallisation, as indicated by the intersections of the vertical arrow. The later leakages from the rocks due to subsequent alteration and surficial processes shown by the wide scatter, and apparent very young ages, are not recorded in the fluorite, calcite, or the chlorite from the granite vein.

Other possible mechanisms

Previous literature envisages isotopic and trace element disturbances as due to mineralisation and hydrothermal fluid circulation driven by high levels of heat generation for up to hundreds of million years after intrusion (Walraven *et al*., 1985; McNaughton *et al*., 1993). However, Cathles *et al.* (1997) indicated that magmato-hydrothermal fluid flow tends to be short-lived, typically lasting for about 1 Ma. Sallet *et al*. (2000), using the equations of Cavazzini (1994), suggested an alternative model for the very high $^{87}Sr/^{86}Sr$ of fluorite in the high-silica early Palaeozoic Tabuleiro granites of the Pelotas batholith in southern Brazil, which yield high and variable initial $^{87}Sr/^{86}Sr$ ratios between 0.72334 and 0.8192. Sallet *et al*. (2000) envisaged that very high $^{87}Rb/^{86}Sr$ in evolving interstitial liquids during crystallization could generate high and variable $^{87}Sr/^{86}Sr$ ratios in the late minerals. We have applied this model to the Bushveld data, but as shown in Figure 15, the $^{87}Rb/^{86}Sr$ ratios in the residual liquid would have to evolve to >10 000 and up to 1 000 000 in rocks crystallizing K-feldspar with $^{87}Rb/^{86}Sr$ of *c*. 100, to generate sufficient ^{87}Sr to produce the ratios seen in the calcite and late fluorite in the time available for crystallization of these late stage granite plutons (< 200 000 years). This model is conceivable if the crystallization time was 1-5 million years, but this appears unlikely given the thermal constraints presented above (Robb *et al.*, 2000; based on the thermal modelling profile of Cawthorn and Walraven, 1998).

Extreme initial $^{87}Sr/^{86}Sr$ ratios within fluorite have been reported by Richardson *et al.* (1990) for the Carboniferous East Kempville greisen-hosted tin deposit of Nova Scotia. There, magmato-hydrothermal cassiterite-topaz ore is crosscut by veins containing apatite, triplite, vivianite and fluorite. The quartz-topaz and biotite monzogranite host-rocks are characterised by high initial ratios (0.729 ± 0.001 and 0.727 ± 0.004) whilst the fluorite and phosphate minerals reflect the unusual chemistry of a high $^{87}Sr/^{86}Sr$ (> 0.8284) post ore-forming fluid. They suggest that either a greisen-derived fluid was modified by reaction with the overlying Meguma metagreywacke, or an extremely radiogenic fluid entered the deposit after ore formation and mixed with the post-ore fluid. The fluorite-bearing granites at Zaaiplaats and Spoedwel intruded into a carapace of Rooiberg Felsite, which is known to be penecontemporaneous with the Bushveld Complex (Walraven, 1997). There are thus no significantly older sediments in the area that can account for high to extreme initial ratios within 1 Ma of the time of intrusion, although in the case of the Buffalo fluorite deposit this mechanism may have contributed to the variability in Sr and Nd as the host is a “leptite” or metasomatically altered sediment, presumably part of the Transvaal Supergroup.

Comparisons with previous work

Crocker *et al.* (1988) presented rare earth data for the four original types of fluorite deposit. For their Vergenoeg type (which includes Buffalo and Zwartkloof) Nd and Sm contents are high, similar to those for primary fluorites in this study. For their secondary types, Nd and Sm are generally low, similar to the data for secondary fluorites in this study. In contrast for their Blokspruit and Zaaiplaats types of fluorite, some samples gave very high Sm and Nd abundances (>20 and > 100 respectively) consistent with our primary magmatic fluorite, whereas others show low Sm and Nd (0.56 ppm and 4.8 ppm, respectively, for a purple fluorite in a cavity with chlorite from Zaaiplaats), consistent with data for secondary fluorites in this study. The results from this study therefore suggest that rather than a mineralogical or locality-based classification we can define two types of fluorite - a primary magmatic fluorite and secondary hydrothermal fluorites. Both types may occur in a simple pegmatitic cavity.

CONCLUSIONS

A late magmatic fluid was responsible for the deposition of disseminated fluorite in granites, stockworks and volcanic pipes. The fluorite has variable, but low $^{87}Rb/^{86}Sr$, low initial $^{87}Sr/^{86}Sr$ and initial $^{143}Nd/^{144}Nd$ of 0.5104. The lowest strontium initial ratio at *c.* 2054 Ma of 0.7166 for a fluorite in granite is probably close to that of the granite magma. This fluid may also have significantly altered the original mineralogy (chloritisation of mica, alteration of feldspars) and thus enhanced the porosity. Evidence of very early alteration of the granite mineral assemblage by the magmatic fluid is provided by mineral separates from a granite vein cutting the Main Zone of the Rustenburg Layered Suite, where chloritised biotite has a R_o ratio of 0.719 and has only retained a fraction of its original Rb, and has an enhanced Sr content.

A different and later hydrothermal fluid exploited the enhanced porosity and produced a totally different generation of fluorite and calcite in open vugs and pegmatites at Zaaiplaats with low $^{87}Rb/^{86}Sr$, high $^{87}Sr/^{86}Sr$ and low Nd (<5ppm). In particular, different coloured fluorites in a miarolitic cavity show an extreme range of Sr initial ratios varying from 0.7199 for a dark-green core to >0.85. Associated late calcite shows even more elevated R_o and variable $^{87}Rb/^{86}Sr$ ratios. This hydrothermal fluid was related to external events, possibly associated with Limpopo tectonism rather than to an internally generated fluid. The strontium isotope data from the late calcite precludes major hydrothermal alteration after *c.* 1950 Ma, otherwise the R_o ratios would be higher. Rb-Sr ages for the granites in the range 1790 ± 114 Ma to 1604 ± 70 Ma therefore most likely reflect low-temperature alkali element mobility and isotopic resetting during exhumation of the Bushveld Complex (Robb *et al.,* 2000), probably by heated meteoric water. Open system behaviour and selective mobility of strontium isotopes, as shown by leaching experiments (Irber *et al.,*1996; Cousins *et al.,*1993; Brantley *et al.*, in press), which can occur to temperatures <120ºC, renders most Rb-Sr whole-rock dating of perthitic granites dubious.

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