

# INFLUENCE OF FLUORINE CONTENTS ON MEASURED $\delta D$ OF LI-FE-MICA

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## INTRODUCTION

Fourteen mica samples from the Neoproterozoic Santa Bárbara tin deposit, Rondônia Tin Province, Brazil were analysed in this study. The Santa Bárbara massif, which hosts the deposit, comprises within-plate A-type, metaluminous to peraluminous rapakivi granites belonging to the Younger Granites of Rondônia Suite (Bettencourt *et al.* 1997). The tin mineralization covers a 500 m by 150 m zone, and is mainly expressed by horizontal to subhorizontal lens-shaped topaz-zinnwaldite-quartz greisen bodies (up to 40 m thick) that define a bedded-greisen cupola model (Sparrenberger & Bettencourt 2000, Sparrenberger 2003).

Thirteen of the mica samples are classified as zinnwaldite according to Rieder *et al.* (1998), while the last one is a muscovite (Sparrenberger 2003). Li-rich micas are typical mineral phases of greisens, differentiated granites and pegmatites, as well as veins of Sn-W-Mo deposits (Cissarz 1927 in Rieder 1970). They are also common in topaz granites that are the youngest intrusive phases in rapakivi granites (Haapala 1977a, b). Their presence results from the increasingly important role of volatiles during late stages of differentiation of granitoids associated with rare-element deposits (Pollard 1983).

Lithium shows positive correlation with fluorine in Li-Al (Foster 1960) and Li-Fe micas (Rieder 1970). Fluorine may substitute for OH to its exclusion in natural trioctahedral micas while in dioctahedral micas the molal ratio F/(OH+F+Cl) rarely exceeds 0.2 (Bailey 1984, Munoz 1984).

## MATERIALS AND METHODS

Mean compositions of the micas studied are shown in Table I. Electron probe microanalysis were performed at the Laboratório de Microsonda Eletrônica of the Instituto de Geociências, Universidade de São Paulo, with a Superprobe JXA-8600, JEOL microprobe. Analytical conditions involved 15 kV voltage and a 20.1 nA beam of 10  $\mu$ m diameter. Chemical analysis employing acid attack and ICP-AES for lithium determination were performed at the Laboratório de Química e ICP-AES of the Instituto de Geociências, Universidade de São Paulo.

Table 1 - Mean compositions of mica samples studied.

SAMPLE	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	Li <sub>2</sub> O	K <sub>2</sub> O	F	Cl
AM-14A	40.849 (0.422)	0.095 (0.086)	23.104 (0.626)	17.830 (0.462)	1.297 (0.056)	0.055 (0.019)	0.755 <sup>a</sup> 1.204 <sup>b</sup>	9.656 (0.165)	5.342 (1.238)	0.007 (0.009)
AM-35	40.245 (0.374)	0.045 (0.010)	22.215 (0.229)	19.422 (0.452)	1.178 (0.084)	0.008 (0.007)	0.504 <sup>a</sup> 1.123 <sup>b</sup>	9.475 (0.077)	5.202 (1.346)	0.048 (0.013)
AM-52	35.217 (0.481)	2.802 (0.145)	20.530 (0.586)	27.270 (1.024)	0.349 (0.020)	1.400 (0.119)	0.084 <sup>a</sup> 0.313 <sup>b</sup>	9.335 (0.208)	1.985 (0.331)	0.339 (0.018)
AM-53	38.886 (1.203)	0.622 (0.123)	20.740 (1.336)	22.612 (3.827)	0.918 (0.011)	0.319 (0.027)	0.279 <sup>a</sup> 0.861 <sup>b</sup>	9.342 (0.003)	4.736 (0.447)	0.027 (0.013)
AM-108	37.851 (0.881)	1.032 (0.339)	19.981 (0.814)	23.179 (1.196)	0.906 (0.033)	0.246 (0.012)	n.d. 0.761 <sup>b</sup>	9.140 (0.210)	4.600 (0.659)	0.021 (0.010)
AM-130	39.880 (0.198)	0.021 (0.016)	21.130 (0.129)	21.388 (0.628)	0.857 (0.023)	0.014 (0.005)	0.693 <sup>a</sup> 1.867 <sup>b</sup>	9.615 (0.108)	5.571 (0.333)	0.030 (0.023)
AM-134	38.893 (0.498)	0.206 (0.065)	21.875 (0.277)	22.177 (1.221)	0.880 (0.035)	0.048 (0.018)	0.598 <sup>a</sup> 0.913 <sup>b</sup>	9.198 (0.225)	5.010 (0.632)	0.038 (0.028)
AM-145	36.667 (0.704)	1.110 (0.212)	19.737 (0.283)	27.811 (1.102)	0.722 (0.056)	0.271 (0.019)	0.301 <sup>a</sup> 0.558 <sup>b</sup>	9.274 (0.104)	4.173 (0.301)	0.099 (0.050)
AM-307	46.009 (0.537)	0	32.290 (1.039)	3.487 (0.745)	0.626 (0.133)	0.012 (0.011)	0.007 <sup>a</sup>	10.519 (0.194)	0.966 (0.146)	0.002 (0.002)

Values expressed in wt.%. Numbers in parentheses correspond to standard deviation.

a – content of lithium measured by chemical analysis; b – content of lithium calculated according to Tischendorf *et al.* (1997).

Composition of sample AM-213 was considered similar to sample AM-134; compositions of samples AM-168b and AM-74c were considered similar to AM-35; compositions of samples AM-174c and AM-297 were considered similar to AM-130 (see Sparrenberger 2003).

Crushed and sieved rock samples with 60-100 *mesh* grain size were used for mica separation via Frantz Isodynamic Magnetic Separator. Initially, lateral and frontal inclinations of 15° and 20°, respectively, and a 0.5 A current allowed elimination of all the other minerals present. Two or three additional separations at 0.3 or 0.25 A, depending on the mica composition, were employed to exclude mica flakes aggregated with other minerals, and so produce high purity mica concentrates. Such material was cleaned in ultrasonic bath for 20 minutes.

The hydrogen isotope analysis of separated micas, performed at Scottish Universities Environmental Centre (SUERC), involved induction heating to around 1400 °C to cause dehydroxylation. The platinum crucible

was previously degassed under vacuum at an equivalent high temperature, and the mineral heated overnight under vacuum at 120 °C to remove labile adsorbed volatiles (see Fallick *et al.* 1993). Dehydroxylation products which did not condense at -196 °C were conveyed by Toepler pump to the mercury manometer where their yield was measured; they comprised up to 1% of the final total yield. This was to ensure that released H<sub>2</sub> was collected.

The liquid nitrogen coolant around the condensables was replaced by a solid CO<sub>2</sub> slush (at -76 °C) and released volatiles pumped away. Removal of this second coolant and heating of the trap released water and other trapped volatiles which passed through a chromium furnace at 830 °C (see Donnelly *et al.* 2001) with the resultant gases transferred to the manometer by Toepler pump. After measurement of the yield, the Toepler pump was used to quantitatively transfer the gas to a mass spectrometer sample tube.

Initial isotopic analyses of gases released in this way from micas in the present study gave unexpected (both high and low apparent)  $\delta D$  values and low internal precision during assay (Table II). Also, it was apparent from the observations of higher sample than reference gas pressure for a given mass-to-charge ratio 2 ion beam intensity that the released gases were not pure hydrogen. We conclude that the high F contents of the micas led to chemical reactions which have gaseous products that are not totally separated from hydrogen by the cryogenic method described above. A modification was therefore devised whereby the mass spectrometer sample tube was cooled to liquid nitrogen temperature (-196 °C) prior to opening it to the mass spectrometer.

Table 2 - Yield and hydrogen isotope compositions for mica samples studied.

SAMPLE	MINERAL	ROCK	RESULTS						
			CONVENTIONAL METHOD		METHOD DEvised IN THIS STUDY				
			yield <sup>1</sup>	$\delta D^2$	analysis 1 yield <sup>1</sup>	$\delta D^2$	analysis 2 yield <sup>1</sup>	$\delta D^2$	average $\delta D^2$
AM-14A	zinnwaldite	salmon albitized granite	n.d.	n.d.	1.03	-128	0.99	-126	-127±1
AM-35	zinnwaldite	bedded greisen	n.d.	n.d.	1.54	-99	-	-	-99
AM-52	zinnwaldite	syenogranite	-	-	3.49	-118	-	-	-118
AM-53	zinnwaldite	syenogranite	n.d.	n.d.	1.83	-107	1.69	-112	-110±4
AM-74c	zinnwaldite	greisen	1.74	-142	1.50	-105	1.67	-99	-102±4
AM-108	zinnwaldite	albite-microcline granite	0.99	-126	1.01	-92	-	-	-92
AM-130	zinnwaldite	greisen vein	1.12	-184	1.11	-122	1.04	-125	-124±2
AM-134	zinnwaldite	white albite-microcline granite	1.08	-202	0.97	-125	-	-	-125
AM-145	zinnwaldite	albite-microcline granite	-	-	1.55	-93	-	-	-118
AM-168b	zinnwaldite	quartz pod	1.12	-183	1.13	-124	-	-	-124
AM-174c	zinnwaldite	greisen vein	0.80	-170	0.89	-120	0.91	-146	-133±18
AM-213	zinnwaldite	pegmatite	1.04	-180	1.24	-106	-	-	-106
AM-297	zinnwaldite	greisen vein	n.d.	n.d.	1.43	-86	1.47	-117	-102±22
AM-307	muscovite	muscovite vein	2.4	-80	2.57	-102	2.46	-111	-107±6

1 – yield given in  $\mu$ moles/mg.

2 -  $\delta D$  given in ‰ (permil) relative to the international standard V-SMOW (Vienna Standard Mean Ocean Water).

n.d. – no data. See text for explanations.

## RESULTS

In all cases, the sample and reference pressures were then identical. Also, the internal precision of D/H measurement was acceptable (less than 1‰). Of course, if the presumed post-release chemistry has involved removal of hydrogen and isotopic fractionation, the measured  $\delta D$  may differ from the correct mineral value. As can be seen from the duplicate data in Table II, this amended procedure usually resulted in reasonably reproducible  $\delta D$  (5 out of 7 have 1 $\sigma$  of 6‰ or less), but in two cases (AM-297 and AM-174c zinnwaldites) the reproducibility is substantially worse. Note also that the yield values may contain a non-hydrogen component.

Except for sample AM-307, which is a muscovite with fluorine content of less than 1%, all the hydrogen isotope data obtained by the new method envisaged during this study are from 34‰ up to 77‰ higher than the ones measured, when possible, according to the conventional method (Table II).

## DISCUSSION

According to the conventional method, four (AM-14A, AM-35, AM-53 and AM-297) out of twelve mica analyses did not produce acceptable data. Besides, calculated water isotopic compositions (applying Jenkin's 1988 equation for  $\delta D$  and Zheng's 1993 equation for  $\delta^{18}O$ ) of five (AM-130, AM-134, AM-168B, AM-174c and AM-213) out of six samples would have hydrogen isotope compositions much lower than primary magmatic water (*cf.* Sheppard 1986) (Figure 1a).

Mica and whole-rock  $\delta D$  values (assuming that  $\alpha_{H_2O-melt}$  and  $\alpha_{H_2O-mica}$  are similar when melt H<sub>2</sub>O contents are low) (Taylor 1986) as low as -170 to -202‰ can not be explained by any process known to cause hydrogen isotope shift if the normal  $\delta^{18}O$  igneous rock signature (*cf.* Taylor 1968) is maintained. Magmatic degassing can decrease the hydrogen isotope composition of fresh volcanic rocks to approximately -130‰, and also that of

intrusive rocks to approximately -110‰, while subsolidus crystallization of hydrothermal alteration derived minerals and recrystallization of primary magmatic minerals, in the presence of evolved magmatic water, can result in whole-rock  $\delta D$  value of around -140‰ for biotite and/or amphibole-bearing assemblages (Taylor 1988). Decreasing salinity accompanied by halite precipitation is reported to cause fractionation of hydrogen and correspondent mica  $\delta D$  values as low as -141 to -165‰ (Carten *et al.* 1988). Also, hydrothermal alteration of igneous rocks by light meteoric water can not yield such low mica/whole-rock  $\delta D$  values without a corresponding  $^{18}O$  shift (Craig 1963), as observed in fossil meteoric-hydrothermal systems (Criss and Taylor 1986), especially in the presence of a relatively heavy meteoric water as indicated by sample AM-307 (Figure 1).

Much more realistic hydrogen isotope compositions were obtained via the method devised in this study, according to which all the samples show magmatic or close to magmatic  $\delta D$  values (Figure 1b).

A remarkable positive correlation between  $H_2O$  content in micas, represented by the measured yield, and these new data does exist (Figure 2), except for samples AM-52 (chloritized), and AM-307 (muscovite). However, the extent of halogen replacement of hydroxyl in micas is governed by many independent factors besides its activity during mica crystallization (Munoz 1984), so the mica yield is not necessarily proportional to whole-rock  $H_2O$  content. Another complicating factor is the presence of topaz in these rocks, which has unknown effects on the fractionation of hydrogen isotopes in magmatic systems.

Outgassing of earlier fluids from the magma and boiling have been proved to have operated in the system and demonstrated through extensive fluid inclusion studies (Bettencourt *et al.* 2005). These processes might explain the covariance of mica  $H_2O$ - $\delta D$  values. However, the possibility of such a correlation being an effect of substitution of  $F^-$  for  $OH^-$  in these micas, can not be ruled out.

## CONCLUSIONS

The method as devised in this study, in order to overcome the presence of unknown gases during the conventional cryogenic method employed in hydrogen isotope composition determination, proved to be consistent and of utmost importance for the understanding of D/H behaviour in high-fluorine tin-granite systems. Consequently the correct interpretation of the  $\delta D$  values will be substantially affected if these gases are not adequately separated, as proposed in this study.

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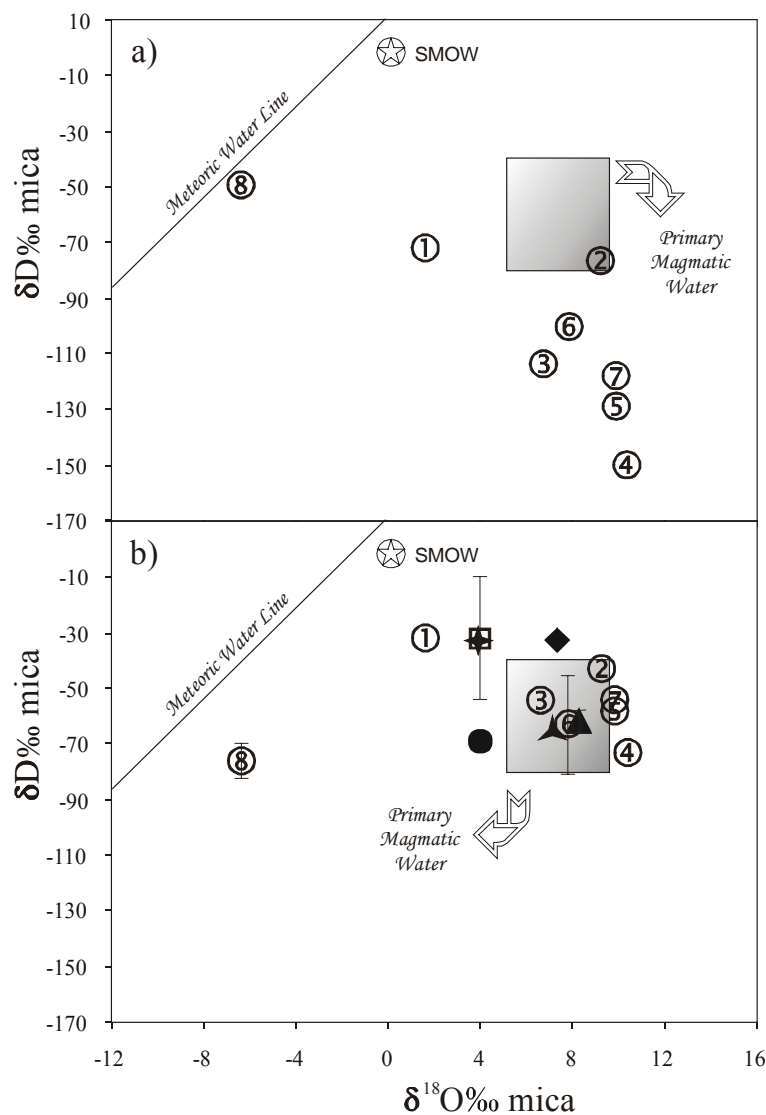


Figure 1. Plot of fluid  $\delta^{18}O$  versus  $\delta D$  derived from analyses of micas in Santa Bárbara deposit according to a) the conventional method and to b) the method devised in this study. Fluid compositions calculated at 603 °C for samples AM-52, AM-53 and AM-108, at 529 °C for samples AM-134, AM-145 and AM-213, and at 380 °C for all the other samples (see Bettencourt *et al.* 2005). Meteoric water line and primary magmatic water box taken from Sheppard (1986). Calculated water isotopic compositions based on equations in Jenkin (1988) for  $\delta D$  and Zheng (1993) for  $\delta^{18}O$ . Data obtained through the new method are plotted with error bars at  $1\sigma$ . Samples which were analysed both by the conventional and new methods have numbered symbols.

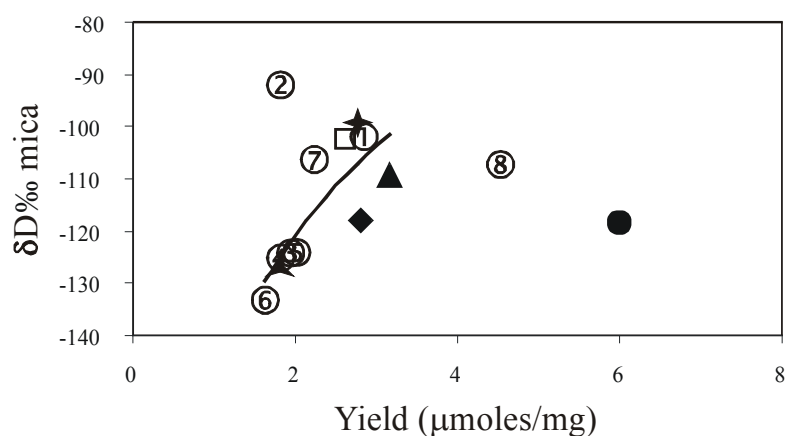


Figure 2. Plot of mica yield versus mica  $\delta D$  for samples of Santa Bárbara deposit showing the positive correlation between mica  $H_2O$  contents and its hydrogen isotope composition. Symbols according to Figure 1.