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## CHARACTERISATION OF SEDIMENTS OF THE TARN FLAT LAKE (ANTARCTICA)

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XRD, INAA and <sup>57</sup>Fe Mössbauer data for a sedimentary core of the small lake of Tarn Flat in the region of Terra Nova Bay are reported and discussed. The lake sediments consist of quartz, muscovite, feldspars, calcite, fluorite and chlorite. Iron is present as Fe(II) in chlorite for about 16%, as Fe(III) up to 74% and in ferrihydrite for the remaining 10% of the total iron content.

The specimens from the border of the Tarn Flat lake contain amphiboles in addition to the silicates found in the sediment but less calcite and fluorite. Their iron chemistry differs from that of the sediment, in particular for the lower Fe(III) content. The specimens from the borders of other lakes present in the region of Terra Nova do not contain calcite or fluorite and differ substantially for silicate composition.

The sediments of the Tarn Flat lake derive from local materials, modified in silicate fraction and enriched in calcite and fluorite.

**Keywords:** Lake sediments; regoliths; Tarn Flat lake; Mössbauer spectroscopy; INAA; XRD

### INTRODUCTION

The water composition of many lakes located in the region of Terra Nova Bay, displayed in Figure 1, has been discussed in many papers [1-7]. It has been reported that the lake chemistry depends mainly on the presence of salts of marine origin and subordinately on the leaching of local materials. The trace elements in the waters do not exhibit anomalous values and the highest content found for some elements has been related to the composition of outcropping metamorphic and granitic formations [2].

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Unlike waters, the lake sediments of the Terra Nova region have received little attention. More data have been reported about the composition of sediments of the lake Vanda, a large lake of 8.46 km<sup>2</sup> and 68.8 m deep, not located in the Terra Nova region but in the Wright Walley [4, 8]. The sediments of lake Vanda contain quartz and feldspars as major constituents, calcite and gypsum, micas and montmorillonite [9]. The presence of montmorillonite and of neo-formed salts as calcite and gypsum differentiate the sediments of the lake Vanda from its surrounding soils (hereafter referred to as regoliths). Differences of this type between sediments and regoliths could be present also in the small lakes located in the Terra Nova region even if these lakes, owing to the low level of deglaciation, are not generally considered as particularly yielding sediments [5].

In order to account for the possible differentiation between lake sediments and surrounding regoliths, the lake of Tarn Flat has been selected for its hydrographic characteristics, among the 70 small lakes and pools of the Terra Nova region. Ice free in the austral summer, the Tarn Flat lake has a surface of about 17 700 m<sup>2</sup> and a maximum depth of 3.9 m. It is located 70 m below sea-level and its distance from the sea is about 35 km. Meltwater is supplied from a drainage area of 2 km<sup>2</sup> and from a glacier of 0.3 km<sup>2</sup>. Water balance is maintained by sublimation of ice from the lake's surface in winter and in summer by feeding another lake of about 42 000 m<sup>2</sup> 10 m lower [7]. Continuous monitoring of many meteorological parameters together with temperature, pH, ionic conductivity of the lake waters has been made from 1991. The monitoring evidenced the permanent absence of ice in the lake 2.5 m below the surface [7]. This finding was so amazing that a possible presence of geothermal manifestations has been taken into account [3].

This paper reports the results, obtained mainly by X-ray diffraction (XRD), instrumental neutron activation analysis (INAA) and <sup>57</sup>Fe Mössbauer spectroscopy, for a sedimentary core of the Tarn Flat lake and for the regoliths collected from the border of some lakes of the region of Terra Nova.

## EXPERIMENTAL

The sampling was performed within the framework of the Italian National Programme for Antarctic Researches, PNRA. A sedimentary core of 17 cm was sampled in January 1994 from the bottom of the lake of Tarn Flat (74°58'S, 162°30'E). The sediment appeared muddy and compact, mixed with sand, with little algal presence and no animal organism. The measurements were performed on nine layers, numbered from the top: 0–2, 2–4, 4–6, 6–8, 8–9.5, 9.5–11.5, 11.5–13.5, 13.5–15.5 and 15.5–17 cm.

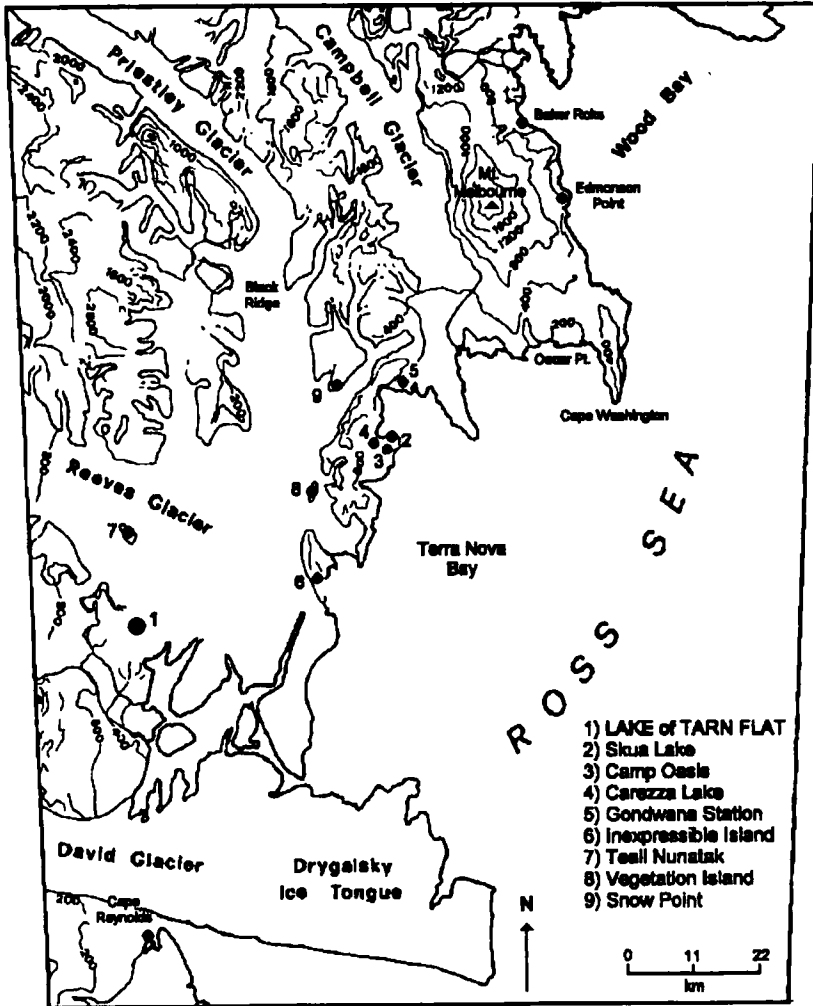


FIGURE 1 Map of the region of Terra Nova showing the position of the lakes taken into account

Regoliths from the border of the lake of Tarn Flat were collected together with additional samples from the borders of Skua Lake ( $74^{\circ}42'S$ ,  $164^{\circ}07'E$ ), Camp Oasis ( $74^{\circ}42'S$ ,  $164^{\circ}06'E$ ), Carezza Lake ( $74^{\circ}42'S$ ,  $164^{\circ}03'E$ ), Gondwana Station ( $74^{\circ}37'S$ ,  $164^{\circ}13'E$ ), Inexpressible Island ( $74^{\circ}52'S$ ,  $163^{\circ}43'E$ ), Teall Nunatak ( $74^{\circ}50'S$ ,  $163^{\circ}33'E$ ), Vegetation Island ( $74^{\circ}47'S$ ,  $163^{\circ}39'E$ ) and Snowy Point ( $74^{\circ}35'S$ ,  $163^{\circ}49'E$ ). The position of these small lakes in the region of Terra Nova is shown in the map of Figure 1. The samples were characterised by various analytical techniques without pre-treatments.

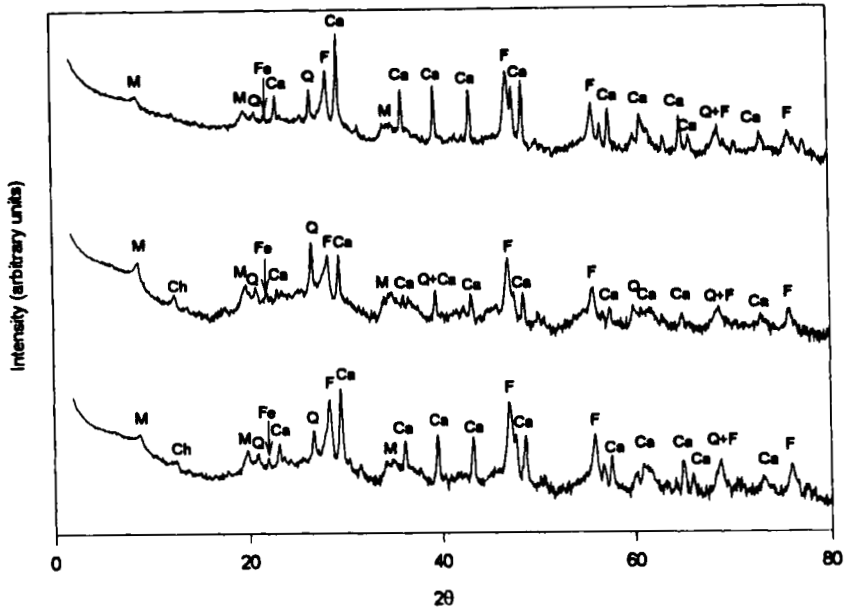


FIGURE 2 XRD pattern for the sedimentary layers of the Tarn Flat lake: 0–2 cm, 8–9.5 cm and 15.5–17 cm (from top to the bottom) (Q = quartz, Ca = calcite, F = fluorite, Fe = feldspar, M = muscovite, Ch = chlorite)

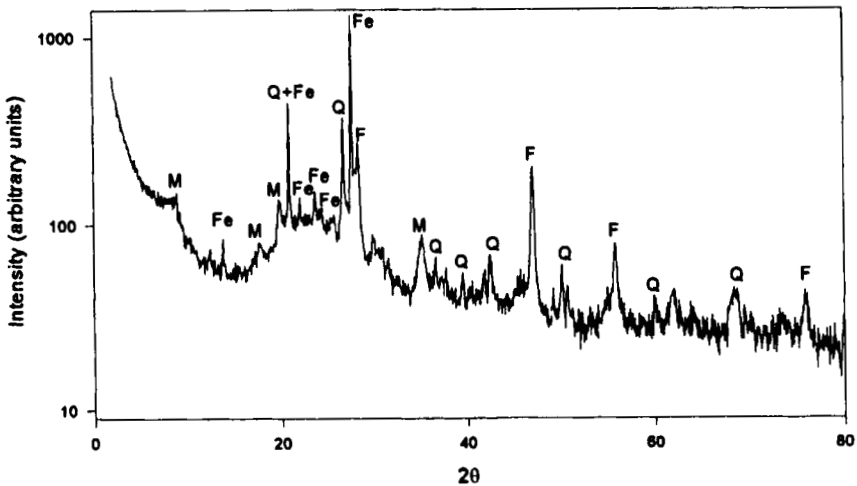


FIGURE 3 XRD pattern for the top layer of the sediment of the Tarn Flat lake after attack with HCl 0.1 M for 4 h (Q = quartz, F = fluorite, Fe = feldspar, M = muscovite)

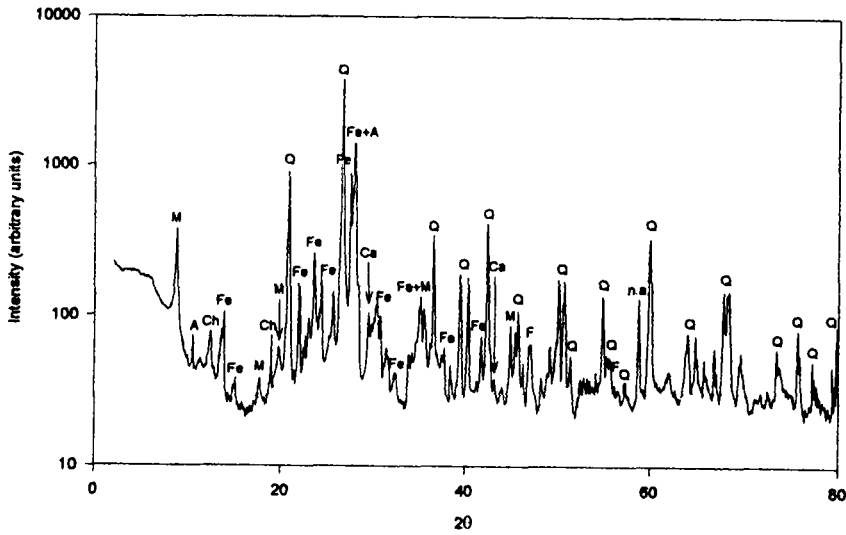


FIGURE 4 XRD pattern for a regolith of the border of the Tarn Flat lake (Q = quartz, Ca = calcite, Ch = chlorite, F = fluorite, Fe = feldspar, M = muscovite, A = amphibole)

TABLE I Mineralogical species detected by XRD in regoliths close to the borders of the reported lakes in Terra Nova region. (Pyroxenes, amphiboles, biotite and chlorite have been confirmed by Mössbauer spectroscopy)

	Quartz	Feldspars	Pyroxenes	Amphiboles	Biotite	Chlorite	Muscovite	Calcite	Fluorite
<b>Tarn Flat</b>	+	+		+		+	+	+	+
<b>Skua Lake</b>	+	+					+		
<b>Camp Oasis</b>	+	+		+	+	+	+		
<b>Carezza Lake</b>	+	+	+	+		+			
<b>Gondwana Station</b>	+	+		+	+	+			
<b>Inexpressible Island</b>	+	+		+	+	+	+		
<b>Teall Nunatak</b>	+	+		+		+			
<b>Vegetation Island</b>	+	+		+	+	+	+		
<b>Snowy Point</b>	+	+		+	+	+	+		

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### **X-ray diffraction**

X-ray powder diffraction patterns were obtained using a Philips PW 2273/20 diffractometer operating with  $\text{CuK}\alpha$  radiation, 25 mA and 40 kV. Some patterns for sediment and regolith from Tarn Flat are displayed in Figures 2–4. The mineralogical species detected in the regoliths are listed in Table I.

### **Ion chromatography**

The ion chromatograms were obtained by using a column AS4A. To prepare the solution, the material was dissolved in concentrated nitric acid. The insoluble fraction was removed and the resulting solution, after dilution and neutralisation, was used for detecting chlorides, fluorides and sulphates.

### **$^{57}\text{Fe}$ Mössbauer spectroscopy**

The Mössbauer spectra were measured with a  $^{57}\text{Co}$  source in a rhodium matrix. The absorbers of about 70 mg were kept at the same temperature as the source (room temperature 293 K or liquid helium temperature 4.2 K). The Mössbauer spectrometer was operated with a sinusoidal velocity wave form. The spectra were fitted with appropriate superpositions of Lorentzian lines using the MOS 90 computer program<sup>[11]</sup>. In this way spectral parameters (such as the electric quadrupole splitting QS, the isomer shift IS and the average linewidth LW in mm/s, together with the relative resonance area A in percent of the total iron) were determined.

### **Instrumental neutron activation analysis**

Three subsamples for every specimen (after grounding, powdering to less than 100 mesh and homogenising) were submitted to a test for homogeneity<sup>[10]</sup>. Samples of about 300 mg were subjected to a first neutron irradiation for 2 h and to a second irradiation, at a thermal flux of  $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ , for 25 h in a 250 kW Triga Mark II reactor. Analogously, the standard SRM 1633a (National Institute of Standards and Technology, USA) and another standard (prepared by adding known amounts of other elements to pure  $\text{SiO}_2$ ) were irradiated. Induced radioactivity was measured, from 3 to 50 days after the irradiation, by a  $\gamma$ -ray spectrometer and a Ge(Li) detector coupled to an analyser-computer. The reliability of the procedure was confirmed by the good agreement between the found and the known elemental contents obtained for the two standards. The elemental contents in mg/g for La, Ce, Nd, Sm, Eu, Gd, Tb, Ho, Tm, Yb, Lu, Hf, Ta, Th, U, Sc, Cr, Ni, Co, Zn, As, Se, Rb, Zr, Sb, Cs, Ba and Fe (in percent) are listed in Table II as an average of three independent determinations. Table II displays the elemental abundance in the nine layers of the sediment and in the typical regolith collected on the border of the Tarn Flat lake.

TABLE II Elemental abundance (in µg/g except for Fe in %) for the nine layers of the sedimentary core of the lake of Tarn Flat. The last column reports the abundance for a typical regolith of its border

	0 - 2 cm	2 - 4 cm	4 - 6 cm	6 - 8 cm	8 - 9.5 cm	9.5 - 11.5 cm	11.5 - 13.5 cm	13.5 - 15.5 cm	15.5 - 17 cm	Regolith
<b>La</b>	42(2)	25(3)	31(5)	40(2)	44(4)	39(2)	45(3)	49(2)	44(1)	31(5)
<b>Ce</b>	56(8)	35(4)	45(6)	57(7)	62(2)	57(5)	66(4)	69(7)	65(3)	58(3)
<b>Nd</b>	35(5)	20.4(3)	26(2)	31(2)	34(4)	29.9(5)	34.8(7)	35(1)	30.1(6)	21.5(4)
<b>Sm</b>	6.90(1)	4.59(3)	6.09(1)	6.22(2)	6.66(5)	6.14(6)	6.90(2)	6.86(4)	6.84(3)	4.57(3)
<b>Eu</b>	0.66(4)	0.44(8)	0.46(1)	0.71(9)	0.76(3)	0.66(3)	0.74(6)	0.86(4)	0.73(1)	0.92(2)
<b>Gd</b>	7.2(8)	4.2(6)	5.9(5)	7.3(7)	6.9(5)	7.0(1)	7.1(3)	7.4(1)	6.9(1)	5.7(1)
<b>Tb</b>	0.78(4)	0.48(1)	0.57(2)	0.94(2)	0.94(2)	0.84(2)	1.01(6)	1.07(3)	0.99(4)	1.01(2)
<b>Ho</b>	1.22(2)	0.53(1)	0.61(1)	0.80(1)	1.16(4)	1.17(3)	1.15(3)	0.99(1)	1.02(2)	1.16(3)
<b>Tm</b>	0.81(1)	0.47(1)	0.50(1)	0.74(1)	1.25(5)	1.02(5)	0.94(1)	1.16(3)	0.98(1)	0.46(1)
<b>Yb</b>	1.53(3)	0.98(3)	1.19(8)	1.56(4)	1.70(7)	1.55(2)	1.76(1)	1.95(3)	1.60(1)	2.1(3)
<b>Lu</b>	0.24(1)	0.33(1)	0.25(2)	0.37(1)	0.44(1)	0.37(1)	0.38(1)	0.37(1)	0.21(1)	0.30(1)
<b>Hf</b>	3.1(1)	1.5(4)	2.2(2)	2.9(1)	3.1(5)	2.4(3)	2.6(3)	3.3(3)	3.4(3)	4.3(6)
<b>Ta</b>	0.92(1)	0.71(1)	0.70(3)	1.02(7)	1.30(2)	1.01(3)	1.30(2)	1.40(1)	1.43(4)	1.16(2)
<b>Th</b>	10.7(4)	6.5(2)	7.9(2)	12(1)	13.6(6)	12.0(2)	14.4(6)	15.9(3)	13.6(1)	11.6(1)
<b>U</b>	7.7(7)	4.7(4)	8.0(1)	6.8(8)	6.3(2)	5.7(3)	6.2(3)	5.7(5)	6.01(8)	4.5(9)
<b>Sc</b>	7.4(4)	4.3(1)	4.9(2)	7.7(6)	8.5(3)	7.6(2)	9.1(3)	10.6(2)	8.8(2)	8.2(4)
<b>Cr</b>	24.0(3)	14.7(8)	17.0(2)	25.0(2)	26.5(4)	25.0(2)	29.0(1)	33.1(7)	26.2(1)	20.8(2)
<b>Ni</b>	75(1)	225(1)	264(1)	124(61)	78(2)	136(1)	77(3)	149(2)	95(2)	13(5)
<b>Co</b>	9.0(1)	5.2(5)	6.2(4)	10.0(1)	11.3(6)	9.4(1)	9.5(2)	10.8(7)	9.8(8)	8.9(2)



	0 - 2 cm	2 - 4 cm	4 - 6 cm	6 - 8 cm	8 - 9.5 cm	9.5 - 11.5 cm	11.5 - 13.5 cm	13.5 - 15.5 cm	15.5 - 17 cm	Regolith
<b>Zn</b>	69(6)	42(7)	45(1)	73(10)	78.6(4)	67.1(9)	79(1)	88(2)	72(1)	60.3(5)
<b>As</b>	9.0(3)	5.9(9)	7.2(2)	6.3(2)	6.6(1)	5.4(1)	5.1(2)	4.7(9)	4.7(2)	1.4(3)
<b>Se</b>	13(2)	9(1)	13.1(8)	14.6(6)	14.7(3)	12.1(2)	11.5(4)	11.5(5)	10.2(4)	2.3(5)
<b>Rb</b>	84.8(8)	53.2(2)	59.4(2)	91(4)	109(5)	88.5(2)	110(8)	122(2)	105(1)	126.7(3)
<b>Zr</b>	188(17)	145.7(4)	184(22)	155(26)	174(27)	131(1)	146(2)	142(2)	154(2)	134.5(9)
<b>Sb</b>	0.39(1)	0.36(1)	0.37(1)	0.37(1)	0.53(1)	0.45(4)	0.46(2)	0.56(2)	0.55(3)	0.14(2)
<b>Cs</b>	4.8(3)	2.9(1)	3.4(1)	5.4(4)	6.0(3)	5.3(3)	6.3(3)	7.4(2)	6.3(4)	4.3(8)
<b>Ba</b>	265(22)	172(1)	207(11)	260(15)	326(30)	272(9)	314(5)	364(10)	299(4)	595(5)
<b>Fe (%)</b>	2.6(1)	1.52(3)	1.73(6)	2.8(3)	3.2(1)	2.65(4)	3.2(2)	3.7(5)	3.2(3)	2.5(3)

## RESULTS AND DISCUSSION

### XRD results

The X-ray diffraction patterns for the top, intermediate and bottom layers of the sediment are displayed in Figure 2 together with the detected species: quartz, calcite, fluorite, feldspar and muscovite. No substantial variation in mineralogy has been evidenced by XRD along the core.

Chlorite scarcely evidenced by XRD has been confirmed by Mössbauer spectroscopy as shown below. Chlorite, one of the most sensitive silicates to weathering, is probably too poorly crystalline to be definitively assigned by XRD. This difficulty is bypassed by using Mössbauer spectroscopy, which sees chlorite from its iron sites, independently from the microcrystalline status. Calcite was confirmed by the disappearance of its XRD peaks after attack of the sediment with hydrochloric acid 0.1 M for 4 h (cf. Figure 3). Fluorite was confirmed by detection of fluoride anions in the ionic chromatography of the solution obtained dissolving the material in nitric acid.

On comparing the XRD pattern for a typical regolith from the border of the Tarn Flat lake (Figure 4) with those of the sediments (Figure 2), the following conclusions are apparent: regolith and sediment differ not only in the amount of calcite, fluorite and silicates but also for type of silicate. In fact the regolith displays more intense peaks attributable to a larger amount of better crystallised quartz, feldspar, muscovite and chlorite and new peaks attributable to amphiboles, undetected in sediments. In addition the regolith exhibits less intense peaks related to the smaller presence of calcite and fluorite.

Taking into account the XRD patterns of the regoliths collected from the border of some lakes of the region of Terra Nova as Skua Lake, Camp Oasis, Carezza Lake, Gondwana Station, Inexpressible Island, Teall Nunatak, Vegetation Island and Snowy Point, no peak, attributable to calcite or fluorite, was identified. Table I lists the different silicates detected by XRD in these regoliths. Chlorite, biotite, amphiboles and pyroxenes have been confirmed by Mössbauer spectroscopy.

### Mössbauer spectra of the sediment

Mössbauer spectra, collected at room temperature, are shown on the left side of Figure 5 for the top and the bottom layers of the sediment. A complete list of the parameters resulting from the least squares fit is compiled in Table III. Two main features are observed in the spectra: the first is the absence of magnetic sextets,

generally due to bulk iron oxides, and the second is the presence of two quadrupole doublets. The first doublet accounts for about 16% of the total iron content and the second for the remaining 84%.

The first doublet is attributed to structural Fe(II) in chlorite since its parameters in Table III (QS 2.58–2.65 and IS 1.11–1.14 mm/s) correspond closely with those reported in the literature (QS 2.62 and IS 1.12 mm/s) [12].

TABLE III Mössbauer parameters at room temperature for the nine layers of the sediment of the lake of Tam Flat and for a typical regolith of its border

Layer (cm)	QS (mm/s)	IS <sup>a</sup> (mm/s)	LW (mm/s)	A <sup>b</sup>	Oxidation State	Fe(II)/Fe(III)
0–2	2.65(2)	1.11(1)	0.40(2)	14(1)	Fe(II)	0.16(2)
	0.68(1)	0.35(1)	0.63(1)	86(1)	Fe(III)	
2–4	2.58(2)	1.12(1)	0.42(2)	16(1)	Fe(II)	0.19(2)
	0.66(1)	0.36(1)	0.64(1)	84(1)	Fe(III)	
4–6	2.61(2)	1.13(1)	0.37(2)	17(1)	Fe(II)	0.20(2)
	0.67(1)	0.36(1)	0.61(1)	83(1)	Fe(III)	
6–8	2.57(1)	1.12(1)	0.37(1)	16(1)	Fe(II)	0.19(2)
	0.64(1)	0.36(1)	0.61(1)	84(1)	Fe(III)	
8–9.5	2.64(1)	1.13(1)	0.36(1)	15(1)	Fe(II)	0.18(2)
	0.64(1)	0.36(1)	0.61(1)	85(1)	Fe(III)	
9.5–11.5	2.61(1)	1.13(1)	0.37(1)	16(1)	Fe(II)	0.19(2)
	0.65(1)	0.36(1)	0.62(1)	84(1)	Fe(III)	
11.5–13.5	2.61(1)	1.14(1)	0.40(1)	17(1)	Fe(II)	0.20(2)
	0.66(1)	0.37(1)	0.64(1)	83(1)	Fe(III)	
13.5–15.5	2.60(1)	1.12(1)	0.34(1)	15(1)	Fe(II)	0.18(2)
	0.66(1)	0.35(1)	0.60(1)	85(1)	Fe(III)	
15.5–17	2.60(1)	1.14(1)	0.40(1)	18(1)	Fe(II)	0.22(2)
	0.63(1)	0.38(1)	0.61(1)	82(1)	Fe(III)	
Regolith	2.56(1)	1.13(1)	0.38(2)	28(1)	Fe(II)	0.75(2)
	1.98(1)	1.10(2)	0.40(1)	15(1)	Fe(II)	
	0.75(1)	0.36(2)	0.60(1)	57(1)	Fe(III)	

a The isomer shift is referred to  $\alpha$ -Fe.

b Relative resonance area in percent of the total iron.

The second doublet has an average linewidth of about 0.6 mm/s (cf. Table III), too broad for a single site. In order to account for this broad doublet, an attempt was made to fit it to two or more spectral components. The results were ambiguous and therefore were not considered further. The presence of montmorillonite,

a possible alteration product, was also ruled out in the fitting procedure [13]. The absence of clay materials in the sediment has been confirmed by XRD in the  $<2\ \mu$  fraction obtained by standard routines. The presence of low-spin Fe(II) in pyrite, contributing to the broad doublet and with Mössbauer parameters comparable to those reported in Table III, was also ruled out. In fact sulphate anions are undetected in ion chromatography excluding any bacterial reduction and any precipitation of pyrite. Such a reduction would be incompatible with the local Eh and the pH ranging from 8 up to 10 in austral summer when the algal photosynthesis is more intense [7].

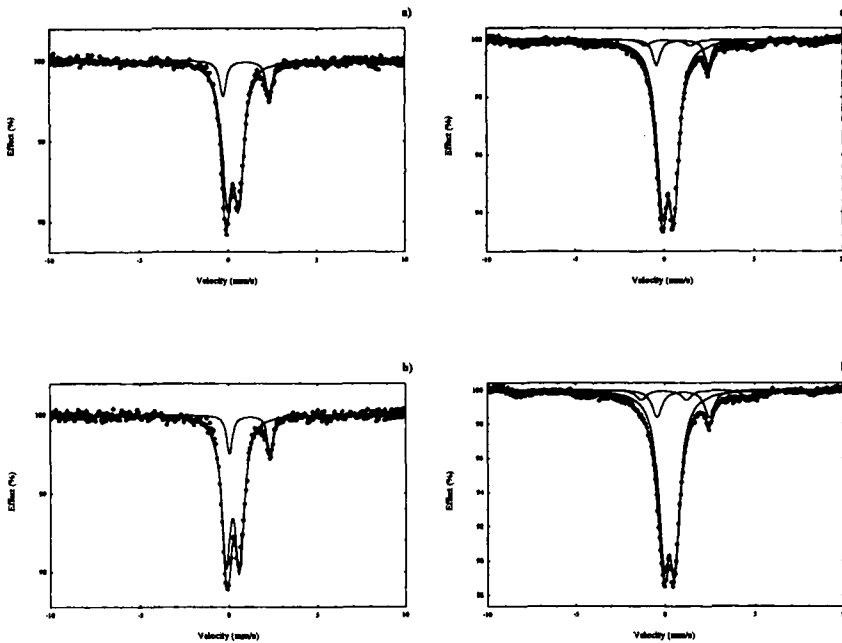


FIGURE 5 Mössbauer spectra for the top layer (a) and the bottom layer (b) of the sedimentary core of Tarn Flat lake. (On the left at room temperature; on the right at liquid helium temperature)

An alternative spectral contribution to the broad doublet could derive from the presence of iron oxide particles small enough to be superparamagnetic at ambient temperature. In fact in finely divided iron oxides, the fluctuations of the electron spin direction may be so fast that the iron nucleus can no longer follow them and therefore the nucleus senses a zero magnetic field. In order to slow down the spin reorientation, Mössbauer spectra were collected at the temperature of liquid helium. The presence of finely divided iron oxide is suggested from the spectra

on the right side of Figure 5, which reveal a magnetic splitting at 4.2 K for a component that was a doublet at ambient temperature. This component could be ferrihydrite since lakes, ground water, stagnant-water soils and drainage areas are considered typical environments in which iron oxide exists as ferrihydrite [14]. It is interesting to note that even the iron oxides of the varnish surface coatings, present in some regions of Antarctica, contain ferrihydrite [15].

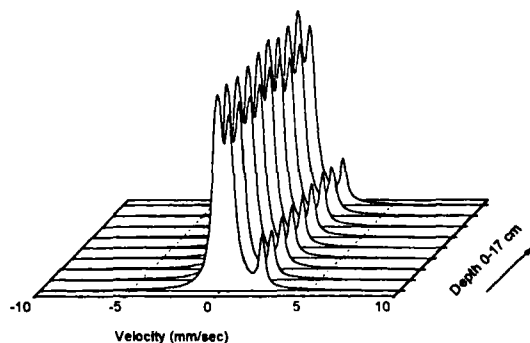


FIGURE 6 Fitted Mössbauer spectra for the nine layers of the lake core. The spectra, collected at room temperature, do not show substantial variation in the iron species along the core

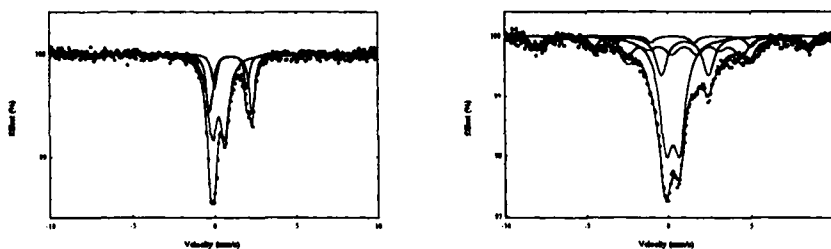


FIGURE 7 Mössbauer spectra of a typical regolith from the border of Tarn Flat lake. (On the left at room temperature; on the right at liquid helium temperature)

The Mössbauer parameters found for the magnetic component (QS  $-0.07$  mm/s, IS  $0.30$  mm/s, magnetic hyperfine field  $B$   $49$  Tesla) agree reasonably with the literature ones for ferrihydrite (QS  $-0.02$ – $-0.01$  mm/s, IS  $0.49$  mm/s,  $B$   $46.5$ – $50$  Tesla) [16]. On the other hand this magnetic component cannot be assigned to hematite, since it usually exhibits hyperfine fields above  $52$  Tesla, nor to goethite since its quadrupole splitting is more negative [17]. It is interesting to stress that some typical peaks of ferrihydrite have been detected by XRD in

the fraction  $<2 \mu$  of the sediment. The broad lines of the sextet in the Mössbauer spectra point to a distribution of hyperfine fields generally present in the spectra of ferrihydrite since it is chemically ill-defined, poorly crystalline and in small particle size. The resonance area of the sextet assigned to ferrihydrite is nearly 10% of the total iron content. This finding indicates that the broad doublet present at ambient temperature with resonance area of about 84% derives from the Fe(III) sites in silicates for about 74% and from Fe(III) in ferrihydrite for about 10 %.

The results obtained for the top and the bottom layers of the sediment can be extended to the intermediate layers. In fact the fitted Mössbauer spectra for the nine layers of the core displayed in Figure 6 show a good similarity in the iron chemistry along the profile of the sediment. This is in agreement with the values, ranging from 0.16 up to 0.22, (cf. Table III), of the ratio Fe(II)/Fe(III), between the Mössbauer resonance areas of the iron sites.

### Mössbauer spectra of the sediment

Taking into account a typical regolith from the border of the lake of Tarn Flat some differences are apparent between its Mössbauer spectrum at room temperature in Figure 7 and those of the sediments in Figure 5. In fact the regolith exhibits three quadrupole doublets instead of two. As shown in Table III these doublets are attributable to Fe(II) and Fe(III) sites.

The first doublet (QS 2.56 mm/s, IS 1.13 mm/s, A 28%) is similar enough in parameters to that found in sediments but the second doublet (QS 1.98 mm/s, IS 1.10 mm/s, A 15%) was not present in the spectra of the sediments. In the fitting procedure both doublets have been related to the presence of the previously detected amphiboles and chlorite. For amphiboles two Mössbauer doublets, attributable to two different Fe(II) sites and with QS of about 2.7 and 2.0 mm/s, have been reported [18]. If chlorite and amphiboles are present, the first doublet overlaps that of chlorite but the second doublet is due exclusively to amphiboles. If the two Fe(III) sites in amphiboles are assumed equally populated, the second doublet with a resonance area of about 15% is assigned to amphiboles whereas the first doublet with a resonance area of 28% is assigned for the same amount to amphiboles (15%) and for the remaining 13% to chlorite

The third doublet observed at room temperature in the spectrum of the regolith is attributed to Fe(III) sites (QS 0.75 and IS 0.36 mm/s). This doublet with a relative resonance area of about 57% differs from of the sediment (about 84%) substantially for the smaller resonance area. Considering the Mössbauer spectrum at 4.2 K of this typical regolith (cf. Figure 7), the magnetic component (QS  $-0.03$  mm/s, IS 0.36 mm/s, B 51.1 Tesla, A 12%) attributable to ferrihydrite is

easily evidenced. The finding implies that poorly crystalline ferrihydrite is present not only in sediments but also in regoliths.

Altogether Mössbauer spectroscopy suggests that there is a real difference in iron chemistry between sediment and regolith of Tarn Flat since Fe(II) and Fe(III) sites are different in number, in parameters and in the relative percentages. In particular, Fe(III) in silicates is about 45% in the regolith whereas it is about 74% in the sediment.

On comparing the Mössbauer spectrum of the regolith from the border of Tarn Flat with those of the regoliths of the border of some lakes in the Terra Nova region, different spectral patterns are observed at room temperature. In fact these last spectra differ in values of the parameters and in number of the quadrupole doublets attributable to Fe(II) and Fe(III) sites, reflecting the local variability in type and amount of the iron-bearing silicates<sup>[19]</sup>. Since the Mössbauer spectra of the various regoliths are specific enough and different from those of the sediment, the Mössbauer parameters in Table III for the sediment probably reflect the alterations due to disgregation, transport and leaching of material of the drainage area of the Tarn Flat lake.

Notwithstanding the variability in the spectral components, all the Mössbauer spectra of the investigated materials, do not exhibit magnetic components at ambient temperature. Instead this magnetic component, attributed to ferrihydrite, is always present in the spectra collected at the liquid helium temperature.

### Major and trace elements

The contents of the major elements for sediments and regoliths, determined by standard Atomic Absorption Spectrophotometry, are similar enough. Their range is 42.3–52.5% for SiO<sub>2</sub>, 9.8–10.7 for Al<sub>2</sub>O<sub>3</sub>, 4.8–9.7 % for CaO, 4.9–5.1% for K<sub>2</sub>O, 1.5–1.8 % for TiO<sub>2</sub> and 1.0–1.1 % for MgO. On the contrary of the major elements, the INAA content of the minor and trace elements in Table II appears more differentiated, in particular between the top and the neighbouring layers in the sediment and between sediment and regoliths.

For comparison purposes the elemental content of the layers of the sediment has been normalised to the mean sediment composition following Bowen<sup>[20]</sup>. These results are displayed in Figure 8. It can be seen that the elemental content for Sc, Cr, Co, Zn, Rb, Sb, Ba, Ta, Fe and for the REE as Ce, Eu, Ho, Tm, is smaller in the Tarn Flat sediment than in the reference one except for Ni, Se and U, which are larger. A substantial alteration in the REE content is also observed for the Tarn Flat sediment normalised to NASC, North American Shale Composition<sup>[21]</sup>. Both comparisons indicate that the Tarn Flat sediment is heavily altered in comparison with the reference standards.

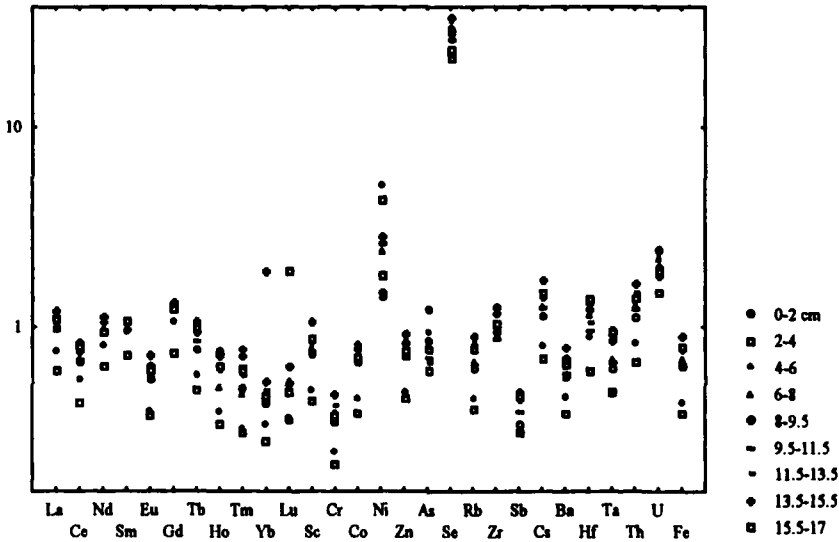


FIGURE 8 Elemental content of the nine layers of the sedimentary core from the lake of Tarn Flat normalised to the mean sediment composition following Bowen [20]

In order to compare sediment and regolith, the elemental composition of the nine layers of the sediment (Table II) has been normalised to that of a typical regolith from the border of Tarn Flat (listed in the last column of Table II). Figure 9 displays that the sediment is richer in Sb, Se, As, Zr and Ni but poorer in Ba, Hf, Rb, and in some REE as Eu, Tb and Yb. In comparison with the lake sediment, the regolith is generally depleted in ions of smaller radius and relatively enriched in ions of large radius. Except for iron, europium and cerium whose chemistry is more complex [22], this finding indicates that the lake sediment is as a collector of defrosting water which transports preferentially elements with small ionic radius leached from the drainage area. Therefore the elemental distribution in the sediment is altered by transport and deposition in comparison with the material of the border.

The strong enrichment of the sediment is also evidenced by comparing the concentrations of the small cations such as  $Zn^{++}$ ,  $Ni^{++}$ , and  $Co^{++}$  (42–88, 75–264 and 5.2–11.3  $\mu\text{g/g}$  respectively listed in Table II) with those reported for the waters of Tarn Flat lake (0.62, 0.192 and 0.033  $\mu\text{g/l}$  respectively) [2].



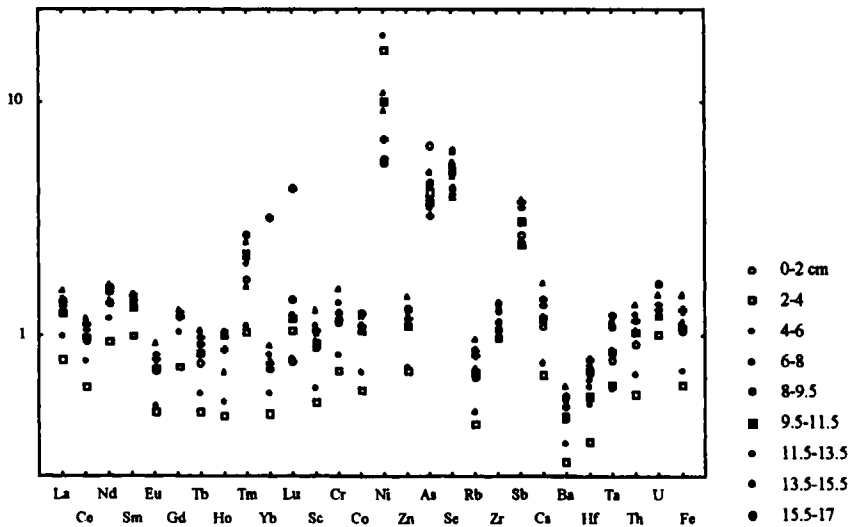


FIGURE 9 Elemental content of the nine layers of the sedimentary core from the lake of Tarn Flat normalised to that found for the regolith from its border

### The composition of the sediment

XRD, Mössbauer and INAA data show significant differences between the sediment and the regolith of the border of the lake of Tarn Flat. Most apparent is the larger presence of calcite and fluorite in the sediment than in the border of Tarn Flat and their absence in the far regoliths of the Terra Nova region (cf. Table I).

Fluorite may derive from dissolution of fluorite of hydrothermal origin contained in granitic rocks present in the drainage area of about 2 Km<sup>2</sup> of the lake of Tarn Flat. Calcite may derive from dissolution of calcite coatings, present in the region of Terra Nova and derived from weathering of bedrock [19]. The low level of fluorite and calcite in the border of the lake of Tarn Flat implies their dissolution and transport to the lake from the drainage area. Fluorite and calcite can be concentrated in lake waters until precipitation takes place in winter owing to the strong sublimation of the ice cover. The presence of fluorite in sediments explains the high concentration of fluoride ions reported for the waters of the lake of Tarn Flat in comparison with the waters of the other lakes of Terra Nova region [2]. In fact in waters of Tarn Flat lake the concentration of F<sup>-</sup> is 2.0–2.5 mg/l and that of HCO<sub>3</sub><sup>-</sup> 65–75 mg/l [2].

Gypsum was not found by XRD in the sediment and the sulphate anions were not detected by ion chromatography. Thus any significant precipitation of sul-

phates is excluded even in presence of a sulphate level of about 20 mg/l in the waters of Tarn Flat lake [2]. The scarce presence of chlorides detected by ionic chromatography indicates that the salts of marine origin are scarcely present in the sediment. This finding is expected since the distance of the lake of Tarn Flat from the sea is about 35 Km. Consequently the waters of the lake of Tarn Flat, considered of middle salinity in comparison with those of other lakes in Terra Nova region, contain not more than 70–80 mg/l of  $\text{Cl}^-$  [2].

The silicate fraction in the lake sediment derives from defrosting water, ice and aeolian transport after the mechanical disgregation of local material. It seems reasonable to exclude aeolian transport from distant places since the silicate composition of the sediment is related to that of the border of Tarn Flat lake. The detrital material transported on the ice cover may migrate through the cover by melting its way down and may sediment on the bottom of the lake [23].

## CONCLUSIONS

The lake sediment of Tarn Flat contains calcite, fluorite and silicate minerals with a low level of salts of marine origin. The sediment derives from local materials, modified in silicate fraction and enriched in inorganic salts.

In the transformation of the regolith into sediment the mechanical disgregation, the transport and depositional phenomena, the chemical weathering determine substantial alterations in elemental composition, iron chemistry and mineralogy.

The permanent presence of liquid water at the bottom of the lake plays a primary role in the oxidation of Fe(II) located in the silicate minerals of the sediment. In fact the ratio Fe(II)/Fe(III), ranging from 0.16 up to 0.22 in the sediment, increases to about 0.75 in the regolith of the lake border, where the presence of liquid water is only seasonal. However both in lake core and in the regoliths there is enough liquid water to favour the hydrolysis of the neo-formed Fe(III) cations to form ferrihydrite. This poorly crystalline iron oxide, the precursor of hematite, is present in all investigated samples.

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