



Characterization of Spanish River Carbonatite (SRC) for agricultural fertilizer

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Abstract

Carbonatite is an igneous rock that is composed mainly of carbonate minerals and silicates. It is recently applied as fertilizer due to its high content of calcite and dolomite. This study presents a physical and chemical characterization of the Spanish River Carbonatite (SRC) and its application as fertilizer is tested. The chemical composition obtained by X-ray fluorescence and Energy Dispersive X-ray analyses indicates that Ca, Fe and Si are the main contained elements. Calcite and SiO₂ are the principal mineralogical phases as detected by X-ray diffraction. Fourier transform infrared spectroscopy confirms the presence of calcite, silicates and also organic material and water. It also suggests the presence of vermiculite. Thermal analysis reveals only a one-step reaction that corresponds to the decomposition of calcite. Mössbauer spectroscopy performed at room temperature do not show magnetic order between the iron moments instead it shows Fe²⁺ and Fe³⁺ doublets in M1 and M2 octahedral sites belonging to vermiculite. At 50 K, we observe that the isomer shift increases their values due to the second order Doppler shift. SQUID magnetometry measurements reveal that most of the sample contains paramagnetic domains assigned to the silicates and calcite components. However, under low applied fields, a tiny signal for Verwey transition appears at 124 K (suggesting the presence of magnetite) although screened by the strong paramagnetic signal of the main components. The SRC has been tested as potential fertilizer on sweet cucumber (*Solanum muricatum*) which responded positively to the application to carbonatite as an amendment, expressing itself in high foliar biomass.

Keywords Carbonatite · Spanish River carbonatite · Vermiculite · Fertilizer · Mössbauer · SQUID magnetometry

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1 Introduction

Carbonatites are igneous rocks that contain >50% of carbonate minerals and <20% of SiO₂ in their composition. Depending on the dominant mineral, which could be calcite (CaCO₃), dolomite (CaMg(CO₃)₂) or iron-rich, carbonatites are classified as calciocarbonatites, magnesiocarbonatites and ferrocyanatites [1, 2]. Other minerals found in carbonatites are ankerite, siderite, bastnasite, pyrrhotite, sylvite, vermiculite, etc. [3].

Since carbonatites rocks have majority carbonate minerals such as calcite and dolomite, and silicate minerals to a lesser extent, they could be used as potential fertilizers [4]. In fact, there are studies about its use as a fertilizer [5, 6]. Boreal Agrominerals Inc. commercializes a calciocarbonatite named “Spanish River Carbonatite” (SRC) which originated by the impact of an asteroid near the Spanish River in Northern Ontario, Canada. The asteroid penetrated 50 km deep into the earth’s crust with an area of influence of 250 km². It is hypothesized that SRC was formed when magma intruded into the overlying bedrock of the area around 2.8 billion years ago [7]. According to Boreal Agrominerals Inc. the composition of SRC consists of four unique parts, all with the same level of importance: 50% calcium carbonate, 25% biotite (potassium mica /pyroxene /vermiculite), 12% apatite (phosphorus) and 13% trace and rare earth elements [7].

James Jones (2016) tested the effects of SRC on field pea (*Pisum sativum*) and found that the soil pH increases to approximately 7.0 and maintained this pH over 42 days, while soils to which only chemical fertilizers were added become more acidic (by 0.5 pH units) [5]. Moreover, the same author claims that the number of microbe colonies per gram in soils treated with SRC is twice higher than in soils with no added SRC. The plant samples were colonized by mycorrhizal fungi, suggesting no negative effects of high SRC concentrations on the beneficial root symbionts [6]. When grown to maturation, plants given a 1:10 ratio (SRC: soil) are claimed to produce seeds with greater dry weights than those given nutrient solutions, even when that solution is supplemented with additional N:P:K fertilizer [5].

In this work, SRC from Boreal Agrominerals Inc. is characterized by complementary physical and chemical techniques and its application as fertilizer is tested. The SRC sample was deeply characterized by scanning electron microscopy, energy dispersive X-rays, X-ray diffraction, X-ray fluorescence, Fourier-transform infrared spectroscopy, simultaneous Thermogravimetric and Differential Thermal analysis and Mössbauer spectroscopy. This was complemented with magnetometry analysis. Its application as a fertilizer was tested on sweet cucumber or pear-melon (*Solanum muricatum*) growth.

2 Experimental

The SRC fertilizer was purchased from Boreal Agrominerals Inc. The samples were analysed as received, without reaction with any other chemical. The scanning electron microscopy (SEM) analysis was performed in a Philips XL30 coupled with a X-ray energy dispersive spectrometer (EDX) from Oxford Inc. The X-ray fluorescence (XRF) analysis was performed on an EDX-720 from Shimadzu. The X-ray diffraction (XRD) measurements were performed on Rigaku Brand diffractometers using both, copper (Cu K α) and cobalt (Co K α) radiations, with $10^\circ \leq 2\theta \leq 90^\circ$, step of 0.02 ° and time of 4 s/step. These measures were carried out to identify the crystallographic phases present in each of the samples.

Fourier-transform infrared spectroscopy (FTIR) measurements were performed in a Perkin Elmer Spectrum RX-1 by averaging 32 scans at a resolution of 16 cm^{-1} in the range of $4000\text{--}400\text{ cm}^{-1}$ using potassium bromide (KBr) pellets. The spectra were obtained with respect to a KBr background collected under the same measurement conditions. The simultaneous thermogravimetric and differential thermal analysis (TG – DTA) was carried out in a LINSEIS STA PT1600 equipment from room temperature (RT) to $1000\text{ }^{\circ}\text{C}$ in air atmosphere and $10\text{ }^{\circ}\text{C}/\text{min}$ heating rate. An alumina crucible (Al_2O_3) with 31.0 mg of sample and empty reference crucible for DTA was used. Mössbauer spectroscopy (MS) was carried out at RT and at 50 K using a radioactive source of ^{57}Co (Rh) of 50 mCi activity and linear velocity. To reach 50 K a commercial compressor cryostat was used. The spectrometer was calibrated from the spectrum of a $\alpha\text{-Fe}$ thin foil. The fitting of the spectrum was performed using the WinNormos software. The magnetic measurements were taken in a DC-MPMS-SQUID magnetometer from Quantum Design inc. The temperature dependence of the magnetization was taken in ZFC and FC modes in the temperature range 5 – 400 K under 50, 500 and 5000 Oe. The applied field dependence of the magnetization was taken in the range $\pm 10\text{ kOe}$ at 5 and 300 K.

The SRC fertilizer was tested on sweet cucumber or pear-melon (*S. muricatum*) growth. The sweet cucumber or pear-melon is a species native from the Andean region, which has been cultivated for several thousand years. Fifty pots of 20 kg capacity each was filled with vermiculite (25%) and farm soil (75%); and four treatments with 1, 3, 5 and 7 g of SRC were applied. Each treatment was repeated ten times.

3 Results and discussions

In Fig. 1(a) a photography of the Spanish River Carbonatite (SRC) sample is shown. It has fine grains, and its characteristics brown colour is because its predominant composition is calcite. Figure 1(b) shows the SEM micrograph of the SRC taken at $479\times$ magnification, revealing small and elongated grains with sizes ranging from 10 to $100\text{ }\mu\text{m}$. The elemental chemical composition performed by XRF (inset Fig. 1(a)) reveals that Ca (42.04%), Si (24.63%) and Fe (27.23%) are the main constituting elements, whereas other elements like K, Ti, Sr, Mn, Cu and Zn are found in minimal amounts (<3%) (See Table 1). Figures 1(c) and (d) show the EDX mapping taken on the selected areas on the sample. Note that the grains are not of the same colour meaning that each one is rich in a specific element. Thus, most of the grains in the micrographs are rich in Si, Ca, and Fe, which is in agreement to the XRF analysis above. The EDX summatory (Sum-EDX) spectra are shown in Figs. 1(e) and (f), respectively. The sum-EDX spectrum shown in Fig. 1(e) was taken over the area marked with a white rectangle in Fig. 1(c) ($215\times 164\text{ }\mu\text{m}^2$ area); whereas, the Sum-EDX spectrum shown in Fig. 1(f) was taken over the whole area of Fig. 1(d) ($309\times 413\text{ }\mu\text{m}^2$ area). The element quantification is given in Table 1. Although C and O exist in the sample, they were not considered during quantification since their signal in the spectra could come from the atmosphere or the carbon tape used as a sample holder. Thus, the main elemental constitution of SRC found by EDX are Si (Fig. 1(c) 34.51 Wt%, Fig. 1(d) 37.72 Wt%), Fe (Fig. 1(c) 39.01 Wt%, Fig. 1(d) 30.52 Wt%), Ca (Fig. 1(c) 19.11 Wt%, Fig. 1(d) 13.90 Wt%) and K (Fig. 1(c) 4.85 Wt%, Fig. 1(d) 14.64 Wt%). Other elements like Ti and Mn are found to a lesser extent (see Table 1). In contrast to XRF, Sr and Zn are not found

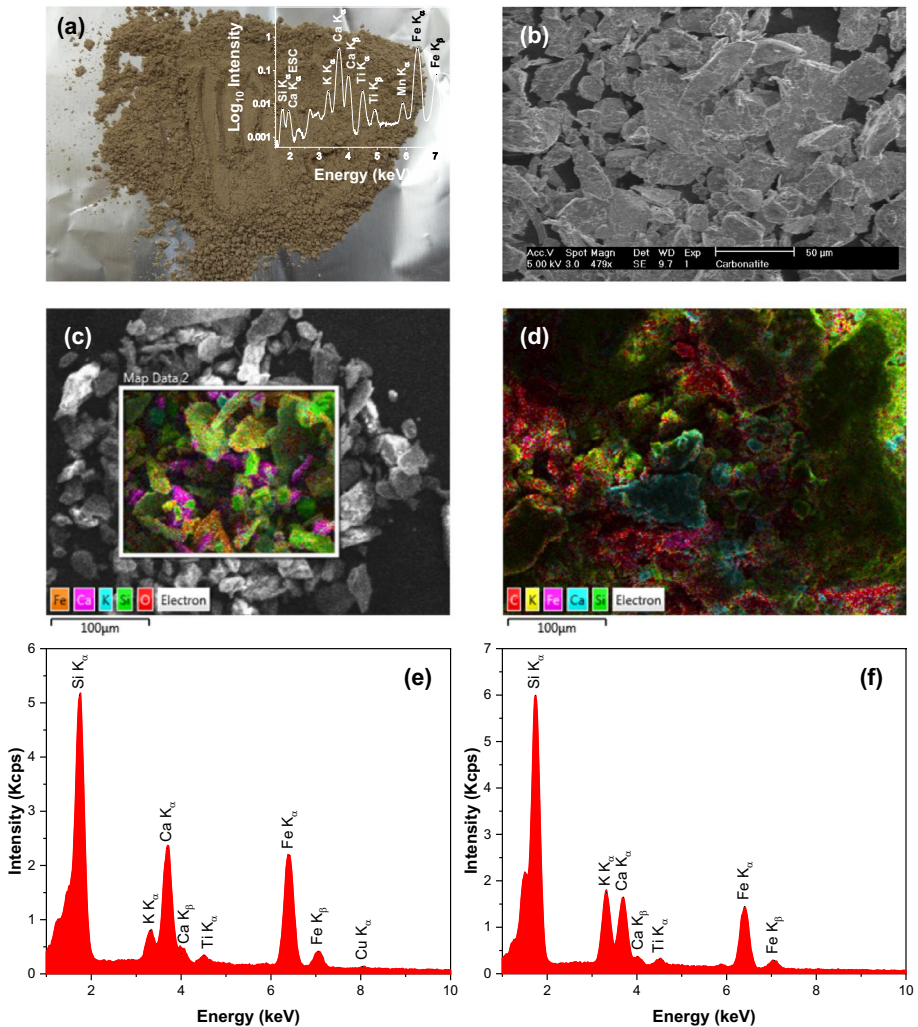


Fig. 1 A photography (a), a SEM micrograph (b), EDX mapping micrographs on small (c) and wide (d) areas and EDX spectra taken on the respective selected areas (e) and (f) of a Spanish River Carbonatite (SRC) sample

by EDX. This is because XRF is more accurate than EDX since the X-rays have a better penetration depth than the primary beam from SEM [8].

According to Boreal Agrominerals Inc., the Spanish River Carbonatite contains calcium carbonate, biotite (potassium mica /pyroxene /vermiculite), apatite (phosphorus) and other rare earth elements [7]. In the present work, both, copper (Cu $K\alpha$) and cobalt (Co $K\alpha$) radiation XRD were used to determine more accurately its mineralogical composition. The XRD are shown in Fig. 2. Note that the XRD are also presented in logarithmic scale in order to reveal possible reflections hidden in the background. The phases identified using both radiations were quartz (SiO_2 , ICSD PDF Card No. 01-085-1780) and calcite (CaCO_3 , ICSD PDF Card No. 01-072-1937) indicating that both are the major components in the sample. Moreover, in agreement with Boreal Agrominerals

Table 1 Chemical composition of Spanish River Carbonatite (SRC) fertilizer taken by XRF and EDX techniques. The quantification does not take into account the C and O

Elements	XRF (%)	EDX (Wt%)	
	Figure 1(a)	Figure 1(c)	Figure 1(d)
Si	24.63	34.51	37.72
K	2.4	4.85	14.64
Ca	42.04	19.11	13.90
Ti	2.21	1.61	1.99
Sr	0.91	–	–
Mn	0.49	–	1.24
Fe	27.23	39.01	30.52
Cu	0.05	0.90	–
Zn	0.05	–	–

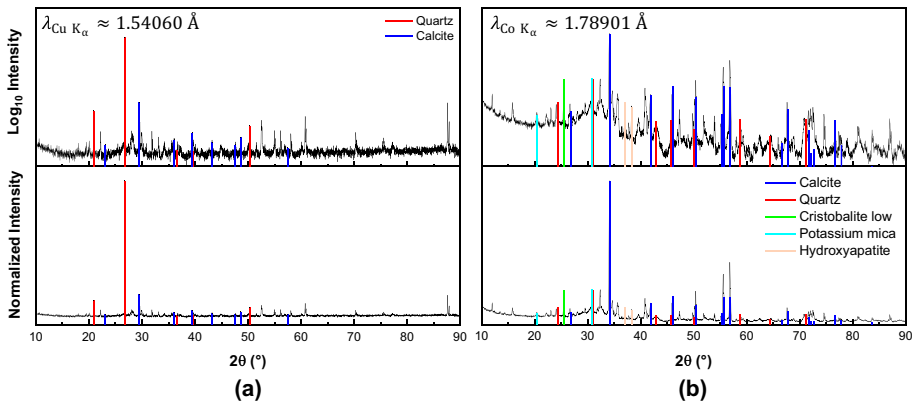


Fig. 2 XRD diffractogram for Spanish River Carbonatite (SRC) fertilizer using both, copper (a) and cobalt (b) radiation with normal (below) and logarithmic (above) intensity

Inc., the biotites potassium mica ($KAl_3Si_3O_{11}$, ICSD PDF Card No. 00-046-0741) and apatite hydroxyapatite ($Ca_5(PO_4)_3(OH)$, ICSD PDF Card No. 01-073-0293) are also found in the XRD obtained with Co-radiation. This is in addition to the better identification of SiO_2 (ICSD PDF Card No. 01-076-0935) as cristobalite low. This is because, in contrast to Cu radiation, Co radiation offers a better diffractogram since it prevents the fluorescence effect in many atoms [9]. However, XRD is not sufficient for detecting possible iron oxides existing in small amounts in the sample. As discussed below, Mössbauer spectroscopy and magnetometry could reveal more information about possible iron oxides or iron silicates contained in the sample.

The FTIR spectrum of SRC is presented in Fig. 3. The bands at 712, 875, 1396-1438, 1798 and 2512 cm^{-1} are associated with the bending and asymmetric/symmetric stretching vibration of C–O and C=O bonds of $CaCO_3$ [10, 11]. The bands at 463, 646 and 1013 cm^{-1} can be attributed to Si–O–Si bending vibration, O–Si–O bending vibration and asymmetric stretching vibrations of Si–O of vermiculite, respectively [12, 13]. vermiculite has not been detected by XRD above since its main reflection appears at 2θ lower than 10° [11]. The shoulders at 780 and 1079 cm^{-1} are associated with Si–O stretching vibration

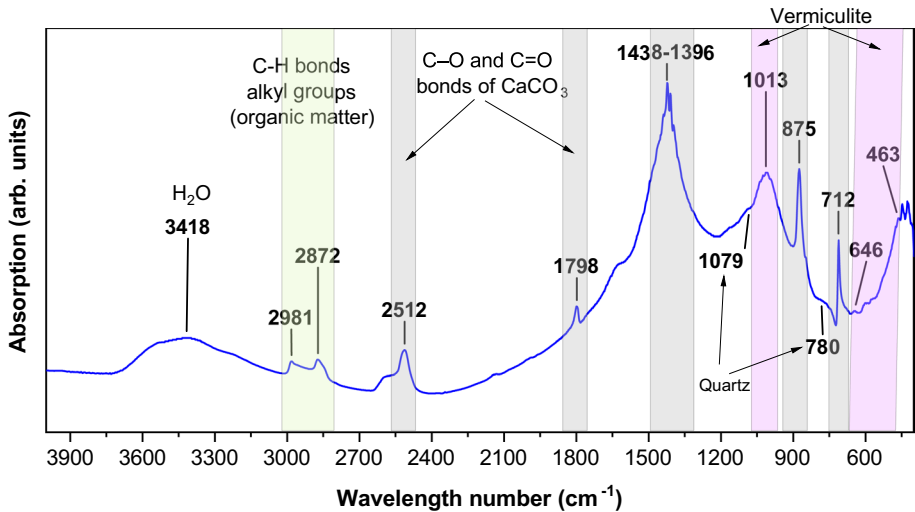


Fig. 3 FTIR spectrum of Spanish River Carbonatite (SRC)

for quartz detected in the XRD [14, 15]. The absorption bands at 2872 and 2981 cm^{-1} are characterized by the asymmetric stretching vibrations of C-H bonds of alkyl groups from organic matter [16, 17]. Finally, the bands at 1624 and 3418 cm^{-1} shows the presence of absorbed water [12, 13].

In the TG curve (see Fig. 4(a)) taken from RT to 600 $^{\circ}\text{C}$, no significant change of mass occurs. However, in the 600 – 830 $^{\circ}\text{C}$ interval a mass loss of 17.9% with a DTG peak at around 800 $^{\circ}\text{C}$ is detected. In the same range of temperature, an endothermic peak at around 808 $^{\circ}\text{C}$ in the DTA curve is observed (see Fig. 4(b) and Table 2) which comes from the heating of calcite (CaCO_3), where de-carbonation and vaporization of carbon dioxide (CO_2) occurs, leaving solid calcium oxide (CaO) [18, 19]. This decomposition of CaCO_3 is consistent with the second drop (680 – 850 $^{\circ}\text{C}$) in the TG curve reported by Wijayarathne W. D. B. [20] for Kawisigamuwa carbonatite from Sri Lanka.

The Mössbauer spectra obtained at RT and at 50 K for the Spanish River Carbonatite (SRC) agromineral are displayed in Fig. 5. At RT, the resulting spectrum consists of a broad absorption composed of many doublets in the central part and does not show any magnetic order of six-split absorption lines, despite the presence of magnetite is suggested by the magnetometry measurements below. The lack of sextets might be related to the dominant paramagnetic phase in the sample. The spectrum was fitted using five doublets and the obtained hyperfine parameters and absorption areas are listed in Table 3. Among all the doublets, two with the high isomer shift (IS), equal to 1.01 and 1.27 mm/s, were assigned to the Fe^{2+} in the octahedral M1 site [21]. Another two doublets of IS equal to 0.44 and 0.38 mm/s have been assigned to Fe^{3+} in the octahedral M2 site [21]. The four doublets labelled as D1, D2, D3 and D4 in the figure are assigned to vermiculite [21–23], which was detected by the FTIR analysis above. In case of D3 doublet there is a dispersity in the quadrupolar splitting (QS) value which could be associated to the overlapping with the other phases. The Fe^{3+} doublet (D5) with Relative Absorption Area (RAA) of 30.8% and hyperfine parameters of IS=0.40 mm/s and QS=0.37 mm/s might be associated with a non-magnetic iron silicate present in the sample.

Fig. 4 Thermal Analysis (TG – DTG/DTA) for Spanish River Carbonatite (SRC) sample, from RT to 1000 °C

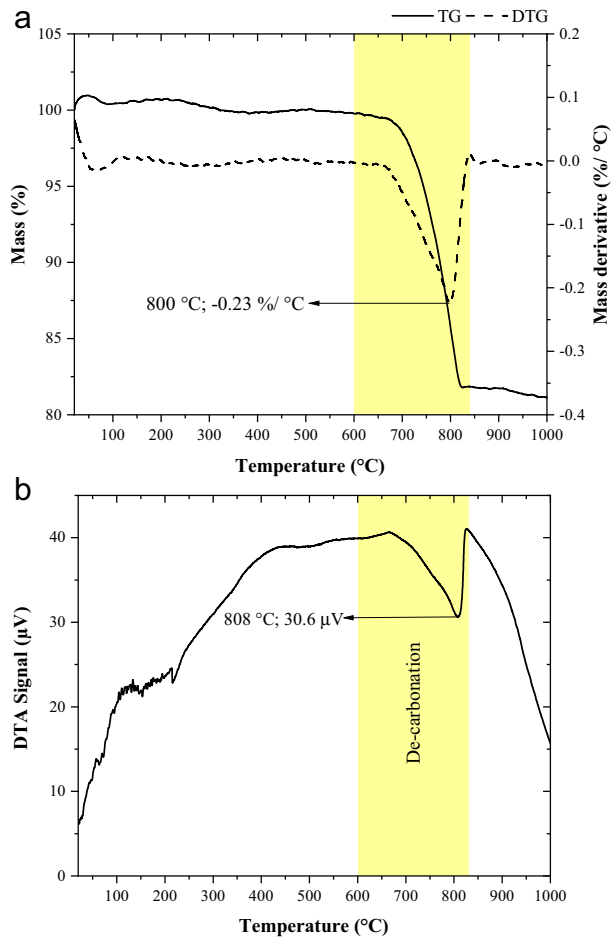


Table 2 Characteristic TG – DTG/DTA parameters for a Spanish River Carbonatite sample

Temperature range	600 °C – 830 °C
Mass loss	17.9%
DTG peak	800 °C
Maximum mass loss rate	-0.23%/ °C
DTA peak	808 °C
DTA Signal	30.6 µV
Type of reaction	Endothermic
Reaction	$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \uparrow$

The Mössbauer spectrum obtained at 50 K still displays the lack of sextets. Despite the fact that the presence of a low amount of magnetite is inferred in the sample from the magnetic measurements below, its corresponding hyperfine signals in the Mössbauer spectra should be screened by the majority of non-magnetic phases (e.g vermiculite) present in the

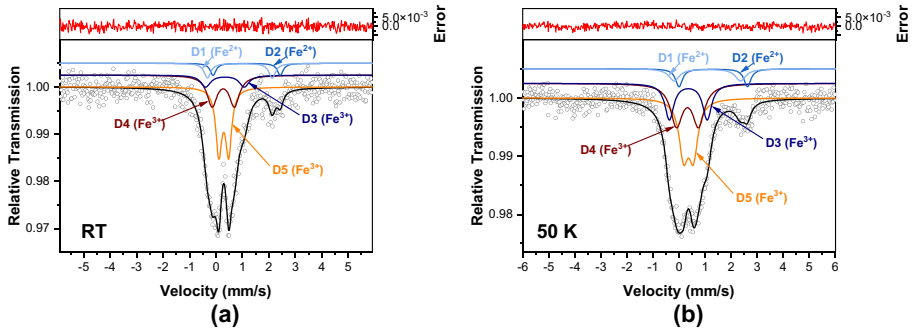


Fig. 5 Mössbauer spectra of the Spanish River Carbonatite (SRC) agromineral at room temperature (RT) and at 50 K measured in the velocity range of -5 mm/s and $+5$ mm/s

Table 3 Mössbauer parameters of Spanish River Carbonatite (SRC) agromineral. The IS values were calculated relative to α -Fe

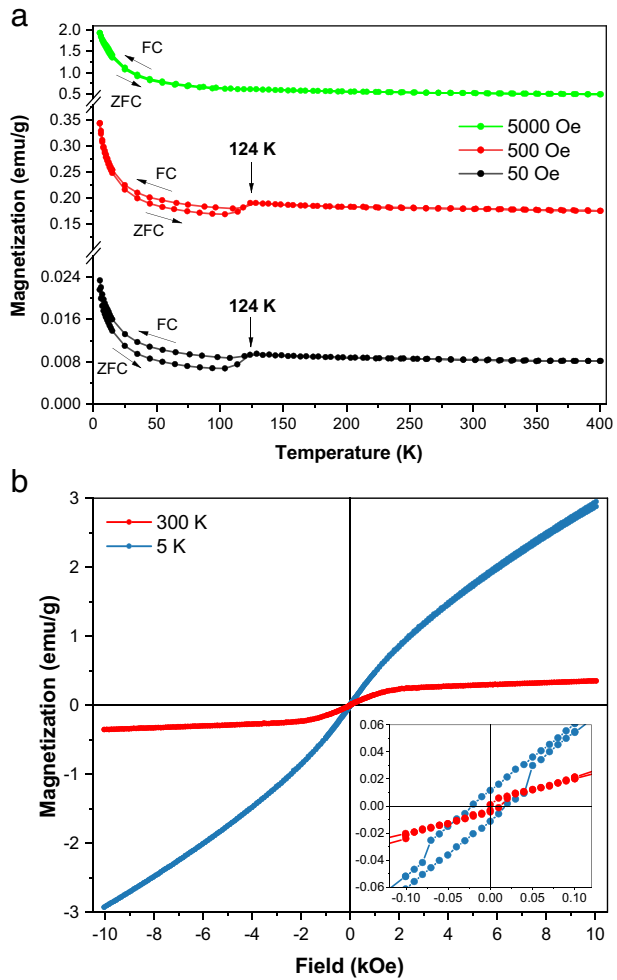
Temperature	Mineral phase	Spectra	Site	IS (mm/s)	QS (mm/s)	W (mm/s)	RAA (%)
RT	Vermiculite	D1	Fe^{2+}	1.01(1)	2.44(7)	0.30(7)	8.8(1)
		D2	Fe^{2+}	1.27(0)	2.53(8)	0.26(6)	5.4(1)
		D3	Fe^{3+}	0.44(8)	1.45(7)	0.44(6)	14.8(7)
		D4	Fe^{3+}	0.38(4)	0.84(1)	0.45(7)	40.1(1)
		D5	Fe^{3+}	0.40(3)	0.37(2)	0.27(4)	30.8(0)
50 K	Vermiculite	D1	Fe^{2+}	1.19(5)	2.54(9)	0.49(2)	8.8(8)
		D2	Fe^{2+}	1.42(1)	2.62(8)	0.32(0)	5.5(9)
		D3	Fe^{3+}	0.46(3)	1.45(4)	0.41(2)	18.6(2)
		D4	Fe^{3+}	0.43(2)	0.84(6)	0.55(4)	37.8(9)
		D5	Fe^{3+}	0.47(0)	0.37(5)	0.42(0)	29.0(2)

sample. Nonetheless, at this temperature the resulting isomer shift increase their values due to the second order Doppler shift. In a similar way, the quadrupolar splitting increases their values due to the increase of the valence contribution to the Electric Field Gradient (EFG). The hyperfine parameters obtained at 50 K are also listed in Table 3.

Figure 6(a) shows the temperature dependence of the magnetization $M(T)$ from 5 to 400 K under 50, 500 and 5000 Oe applied fields. Under the highest applied field (5000 Oe) the ZFC and FC curves overlap, and the sample shows only a paramagnetic behaviour in all the range of temperature. On the other hand, under lower applied fields (500 and 50 Oe) a magnetic transition around 124 K is observed which could correspond to the Verwey transition of the magnetite.

The magnetization vs external applied field $M(H)$ loops from -10 to 10 kOe at 300 and 5 K are shown in Fig. 6(b). Note that under high applied fields, the values of the magnetization increase when the temperature decreases, which is typical of paramagnetic materials. Under low applied fields the loop obtained at 5 K presents a very weak hysteresis (see inset) which is assumed to be caused by the ferrimagnetic signal from the magnetite. These results indicate that the amount of magnetite is very small to be detected by the other

Fig. 6 Magnetization vs temperature obtained under 5000, 500 and 50 Oe applied fields (a) and magnetization vs external field at 5 and 300 K (b) of a Spanish River Carbonatite (SRC) sample



presented techniques above, but from its ferrimagnetic behaviour by the SQUID sensor. In fact, SQUID sensors can detect magnetization signals as small as 10^{-7} emu. In other words, most of the sample is paramagnetic because of the high amount of carbonate and silicates and screening the ferrimagnetic signal of the magnetite due to its tiny amount.

According to the technical data sheet of Spanish River Carbonatite (SRC), this is highly compatible with all recognized fertilizers; such as Urea, Nitrates, Sulfates, and Carbonates, and even more to those organic ones such as compost, humic and fulvic acids, island guano, winter guano, chicken manure etc. It is claimed by Boreals Agrominerals Inc. that it can potentially act as catalysts and recommended as an amendment and random in fertilizer mixtures that contain N, P, K, Mg, Bo, Zn, Mn. In the present work, the SRC is tested as fertilizer on sweet cucumber (*Solanum muricatum*) as shown in Fig. 7. Figure 7(a) shows a panoramic view of fifty pots of 20 Kg each, where sweet cucumber (*S. muricatum*) were treated with SRC as fertilizer. The pots also contain vermiculite (25%) and farm soil (75%) and 4 treatments of SRC were applied: 1, 3, 5 and 7 g. The most appropriate treatment was found to be 5 g of SRC, producing



Fig. 7 (a) Panoramic view of Spanish River Carbonatite (SRC) treatments on sweet cucumber (*Solanum muricatum*), as a fertilizer. (b) Response of sweet cucumber to the application of Spanish River Carbonatite (SRC). A) with SRC and B) Control

greater growth in stem and leaves. Figure 7(b) shows the response of the sweet cucumber plant with shown most appropriate application of SRC. It is labelled as A in the image, whereas the control plant is labelled as B. It is noted that the plants responded positively to the application of Spanish River Carbonatite (SRC), as an amendment, expressing itself in higher foliar biomass.

4 Conclusions

A Spanish River Carbonatite sample was characterized by different techniques. The SEM analyses indicate that the morphology of the samples exhibits small and elongated grains with sizes from 10 to 100 μm . The chemical composition obtained by EDX and XRF revealed the main elements are Ca, Si and Fe. The XRD analyses obtained by both, Cu- and Co- radiations, reveal that the most mineralogical compositions are calcite and quartz. The FTIR spectroscopy suggests that the band at 1013 cm^{-1} can be attributed to asymmetric stretching vibrations of Si-O of vermiculite. The thermal analysis indicates the decomposition of calcite at around $600 - 830\text{ }^\circ\text{C}$. All these techniques indicate that the SRC corresponds to a calciocarbonatite type. The Mössbauer spectroscopy obtained at RT and 50 K display lack of sextets that must be related to the dominant paramagnetic phases in the sample. Besides it presents five doublets; four of them are associated with vermiculite sites and one to a non-magnetic iron silicate. The magnetometry analysis reveals that most of the sample is paramagnetic due to the high amount of quartz and calcite. A small Verwey transition signal appears in the $M(T)$ curves obtained at around 124 K under low applied fields although is screened by the paramagnetic signal of the other components and it has not been detected by the other techniques due to the small amount of magnetite. The SRC has been tested as fertilizer on sweet cucumber (*S. muricatum*) which responded positively expressing itself in higher foliar biomass.

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