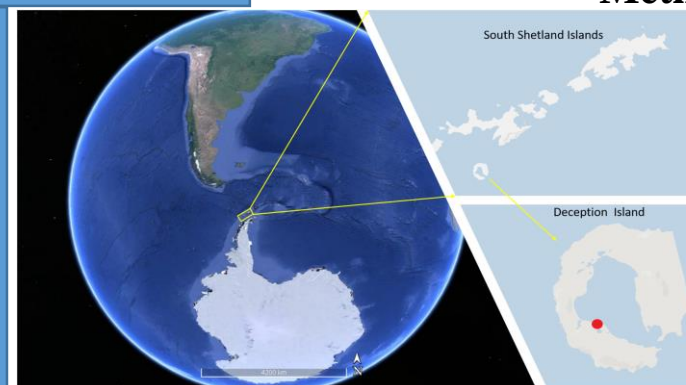




Introduction

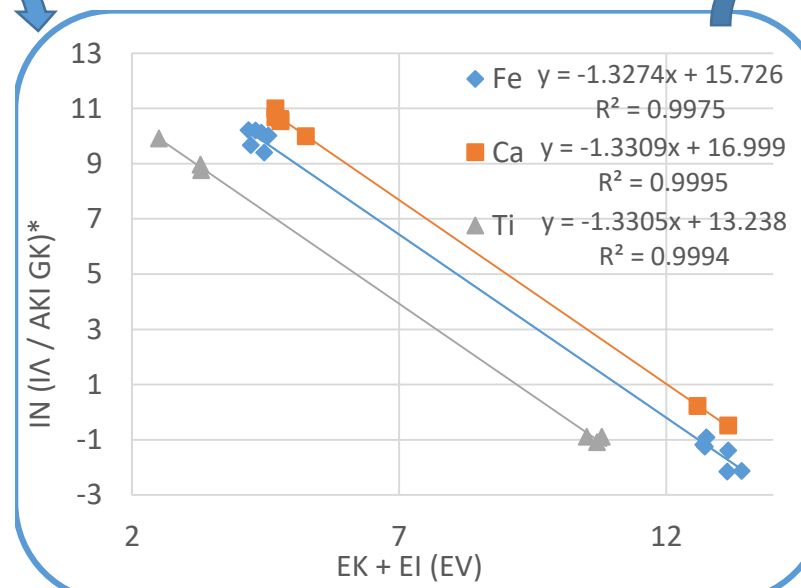
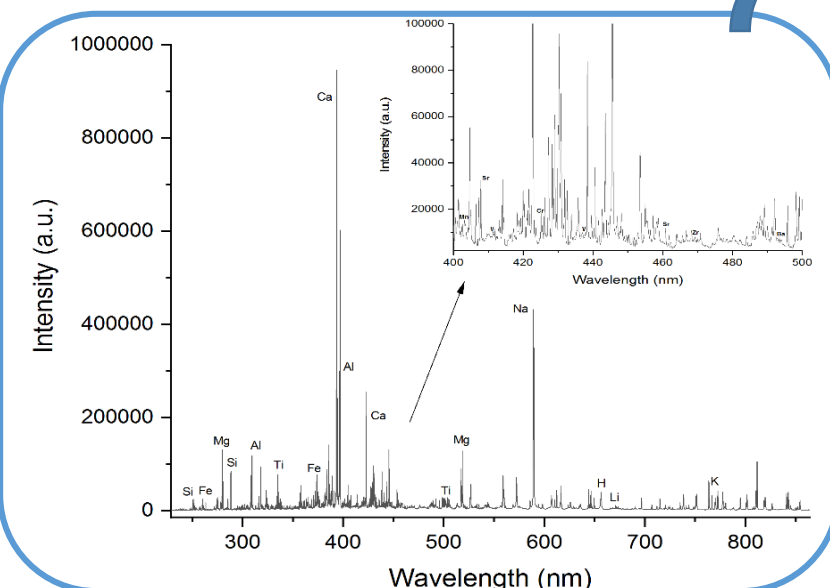
The study of geological samples, such as soils, is one of **Laser-induced breakdown spectroscopy (LIBS)** many applications [1]. Since sometimes the matrix is quite complex, it is complicated to find or manufacture standards for these type of samples. Thus, a good alternative is implementing **Calibration Free (CF)** [2]. When using CF, the physical parameters of the plasma created by the interaction of the laser with the sample, are studied and related with the elements and species that compose it. This methodology has been followed in this work to perform a multielemental **quantitative analysis** of soil samples from **Antarctica**, particularly at Deception Island (Gabriel de Castilla Spanish Research Base, South Shetland Islands).



Methodology

- **6 soil samples** from different parts of Deception Island were taken and analysed.
- Soil samples were pressed as **pellets** for LIBS analysis.
- **120 measurements** per sample
- Delay Time = 1900 ns, Gate Width = 3650 ns, Energy = 45 mJ

Results



Oxides (%)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
SiO ₂	46.3 ± 5	52.7 ± 5.1	54.9 ± 1.2	50.4 ± 1.9	51.3 ± 2.8	49.3 ± 2.7
Al ₂ O ₃	19.1 ± 1.7	18.2 ± 1.8	17.2 ± 0.8	19.4 ± 0.6	18.9 ± 2	20.9 ± 1.4
Fe ₂ O ₃	11.8 ± 1.4	9.9 ± 1.4	9 ± 0.2	9.7 ± 0.3	9.8 ± 0.7	10.9 ± 0.6
CaO	9.03 ± 1.28	7.7 ± 1.2	7.3 ± 0.5	8.1 ± 1	8.2 ± 0.8	7 ± 0.9
MgO	5.8 ± 1.9	5 ± 1.2	4.5 ± 0.5	4.9 ± 0.2	4.1 ± 0.3	4.3 ± 0.6
Na ₂ O	3.8 ± 0.6	3 ± 0.4	3.5 ± 0.1	3.4 ± 0.4	4 ± 0.3	3.2 ± 0.4
TiO ₂	3.3 ± 0.3	2.6 ± 0.4	3.1 ± 0.2	3.4 ± 0.4	3.1 ± 0.3	3.6 ± 0.4
K ₂ O	1 ± 0.2	0.9 ± 0.4	0.7 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	0.8 ± 0.1

No need of calibration standards. Estimation of **Te** and **Ne** to determine composition. **Ne** was obtained from the hydrogen line.

Te was estimated using the **Saha-Boltzman** plot. Mean of the 6 samples: **Te = 9024 ± 54 K** **Ne = 8.3 ± 0.1 × 10¹⁶ cm⁻³**

LTE verification using Mc Whirther Criterion: $N_e \text{ (cm}^{-3}\text{)} \geq 1.6 \times 10^{12} T_e^{1/2} (\Delta E)^3$

Conclusions

- The samples were mainly composed of the following oxides: SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, TiO and K₂O.
- The results were compared with those provided by ICP-OES analysis obtaining close values for most oxides. For minority elements, the CF-LIBS and the ICP-OES results were within the same order of magnitude in all cases but the chrome case.
- These results show that CF-LIBS can be very useful in the characterization of complex samples, such as soils.

References

- [1] Rai, A.K., Pati, J.K., Rai, A.K., 2020. Chapter 16 - LIBS study of geological samples coupled with chemometric methods, in: Singh, J.P., Thakur, S.N. (Eds.), Laser-Induced Breakdown Spectroscopy (Second Edition). Elsevier, Amsterdam, pp. 369-384.
 [2] Tognoni, E., Cristoforetti, G., Legnaioli, S., Palleschi, V., 2010. Calibration-Free Laser-Induced Breakdown Spectroscopy: State of the art. Spectrochimica Acta Part B: Atomic Spectroscopy 65, 1-14.

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