1. Supplementary material

1.1. Sample selection

Figure S1 Sample E70   **Figure S2** Sample E80   **Figure S3** Sample E90

After the samples were collected, granulometry was made with the electric vibrator and the sieve assembly to obtain the granulometry fractions showed in Figure S4 and Figure S5 respectively.

Figure S4. Assembly electric vibrator and sieves.

Figure S5. Gravimetry fractions.

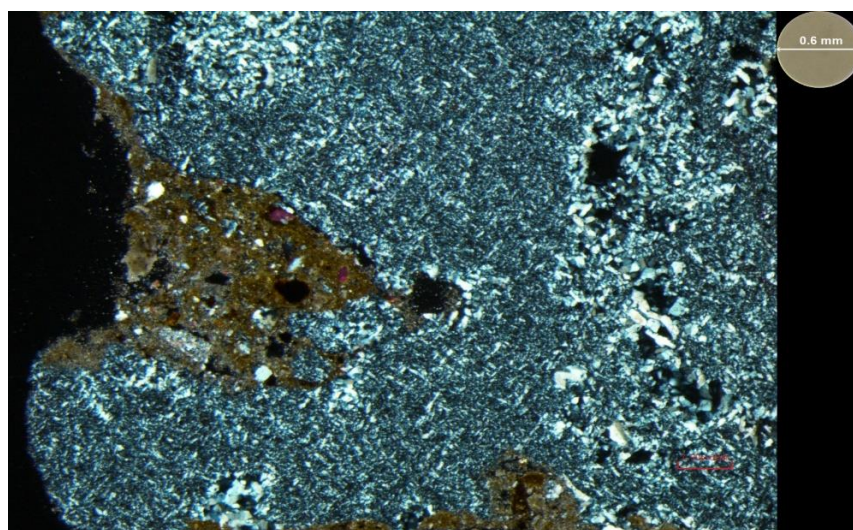## 1.2. Optical microscopy and scanning electron microscopy

Figure S6. Optical microscopy of celestine crystals replacing carbonate, sample E69.
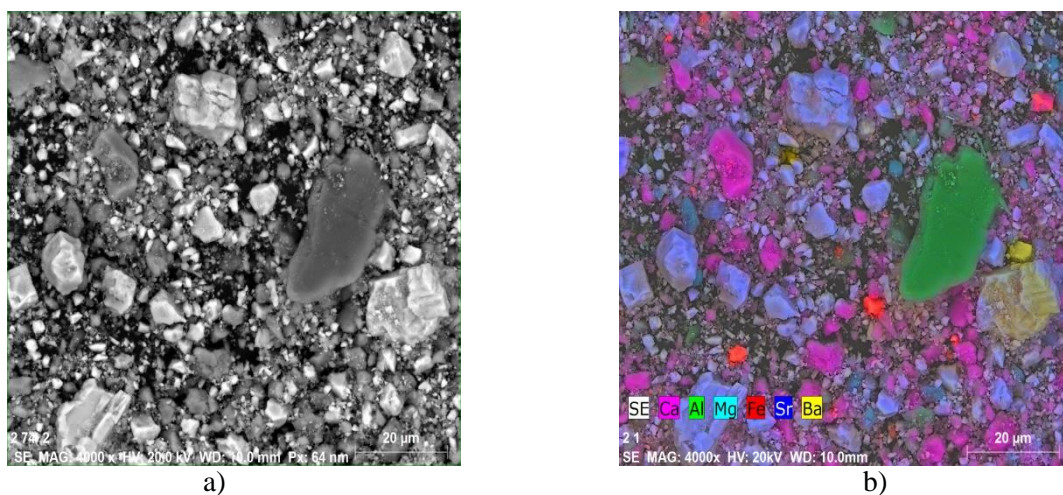

Figure S7. Scanning electron microscopy (a)　and compositional SEM map of　E69 sample (b).

1.3. Granulometry study

Table 1 and Figure S8 shows the % $mass_r$ (retained mass percentage accumulated in each sieve) and f_i (the retained mass in each sieve divided between the total mass). The mass mineral above 10 mm is 12,07 % in E60 sample and the predominant fraction is 5mm-10mm. In contrast, fraction mineral >10 mm is 29,08 % in E69 and 32,52% in E92 and fraction mineral >10 mm is the predominant fraction in both cases. The 90% of mineral mass is above 315 micras in E60 and E69 samples but is above of 100 micras in E92 sample.
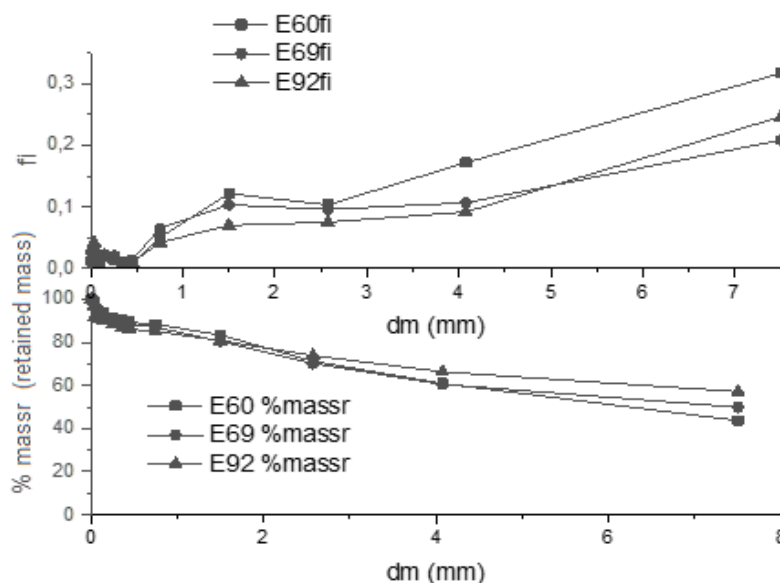
Figure S8. Granulometry results, **% mass_r** and **f_i** to each diameter (mm) in E60, E69, E92 samples.

Table S1 Granulometry results, **% mass_r** and **f_i** to each diameter (mm) in E60, E69, E92 samples.

		E60		E69		E92	
d_m (mm)	f_i	%mass$_r$	f_i	%mass$_r$	f_i	%mass$_r$
>10mm	0	0,121	**12,07**	0,290	**29,08**	0,325	**32,52**
10mm-5mm	7,5000	**0,317**	43,77	0,208	49,93	0,247	57,18
5mm-3.15mm	4,0750	0,172	60,95	0,107	60,60	0,092	66,36
3.15mm-2mm	2,5750	0,103	71,28	0,096	70,18	0,075	73,89
2mm-1mm	1,5000	0,122	83,43	0,103	80,52	0,070	80,88
1mm-500µm	0,7500	0,050	88,40	0,065	87,04	0,042	85,11
500µm-400µm	0,4500	0,009	89,30	0,014	88,42	0,010	86,11
400µm-315µm	0,3575	0,008	**90,12**	0,011	**89,51**	0,008	86,90
315µm-200µm	0,2575	0,015	91,57	0,021	91,58	0,015	88,35
200µm-100µm	0,1500	0,020	93,57	0,022	93,82	0,020	**90,38**
100µm-71µm	0,0855	0,011	94,64	0,009	94,73	0,010	91,40
71µm-50µMm	0,0605	0,010	95,65	0,010	95,71	0,014	92,77
50µm-20µm	0,0350	0,032	98,81	0,031	98,83	0,042	96,93
<20µm	0,0100	0,012	100,00	0,012	100,00	0,031	100,00

This table include the E60, E69, E92 granulometric results

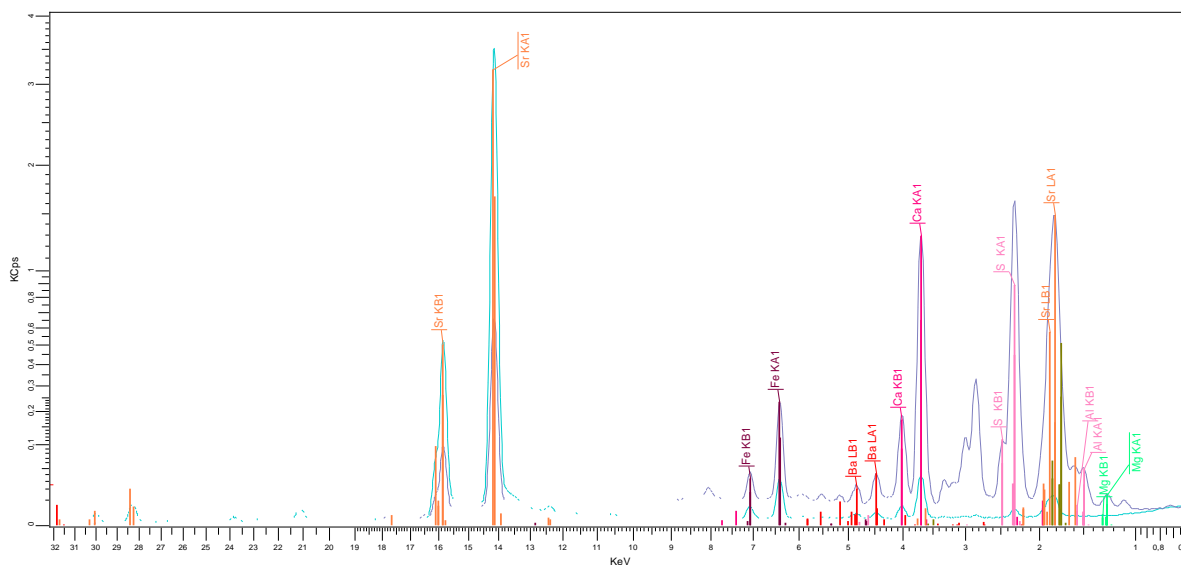*1.4. X-Ray fluorescence and diffraction*

Figure S9. X-ray fluorescence (representative XRF spectra of one of the samples (E69).

1.4.1. X-Ray fluorescence and diffraction

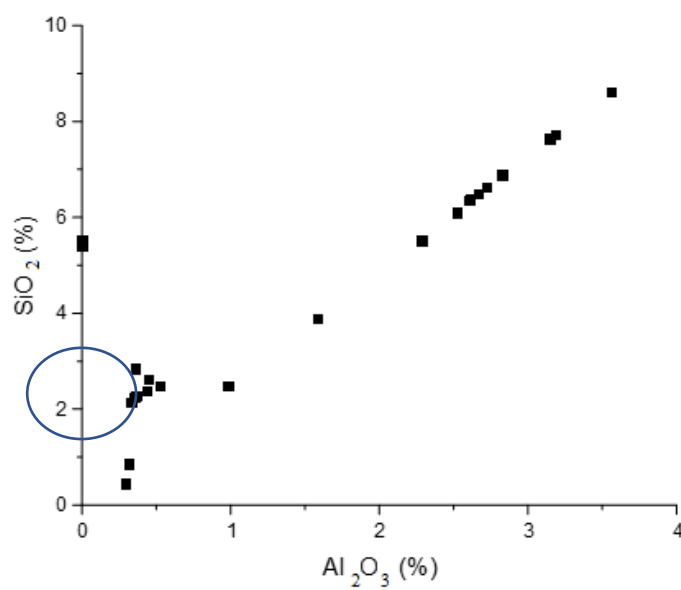Figure S10 shows the relationship between % Al2O3 and % SiO2 obtained in XRF (Table 2).

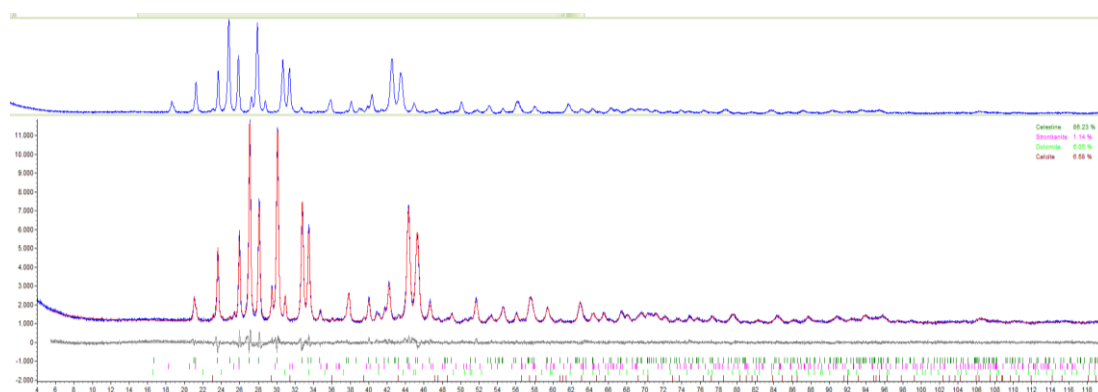**Figure S10.** Correlation Al₂O₃ /SiO₂ obtained in XRF.

Figure S11. Rietveld refinement of X-ray diffraction data used for quantitative mineral analysis.

1.4.2. Study of XRF and DRX correlation

Figure S10 shows the relationship between % Al_2O_3 and %SiO_2 obtained in XRF (Table 2).

Data in Table 2 and Table 4 helped to make the correlation graphics of linear regression (Figure S11, S12). Figure S11 shows the relationship between % $SrSO_4(Ba)$ obtained in XRF and DRX techniques, with a lineal fit whose equation is y= 25,770+1,239 x.　Figure S12 shows the relationship between %$CaCO_3$ obtained by XRF and DRX with a lineal fit equation y= 0,207+1,239 x. The Pearson coefficient showed a high correlation in both mineral phases (Pearson´s up to 0,98).
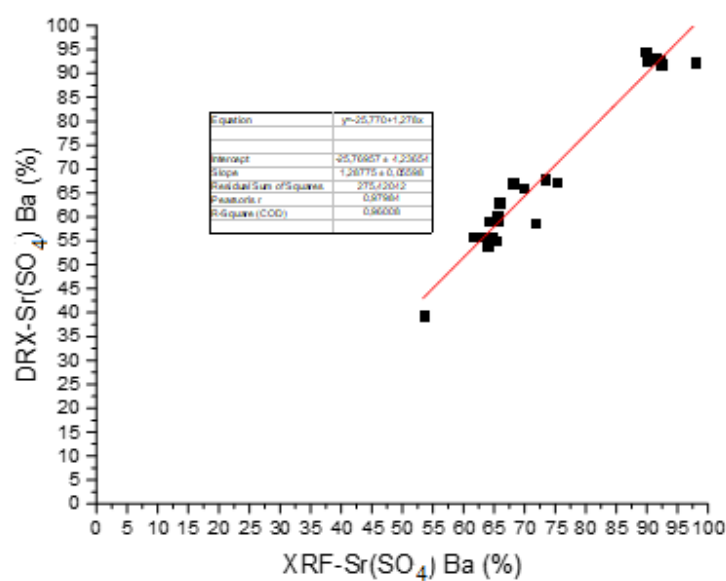

Figure S12. Linear regression model between % $Sr(SO_4)Ba$ obtained by XRF and DRX.
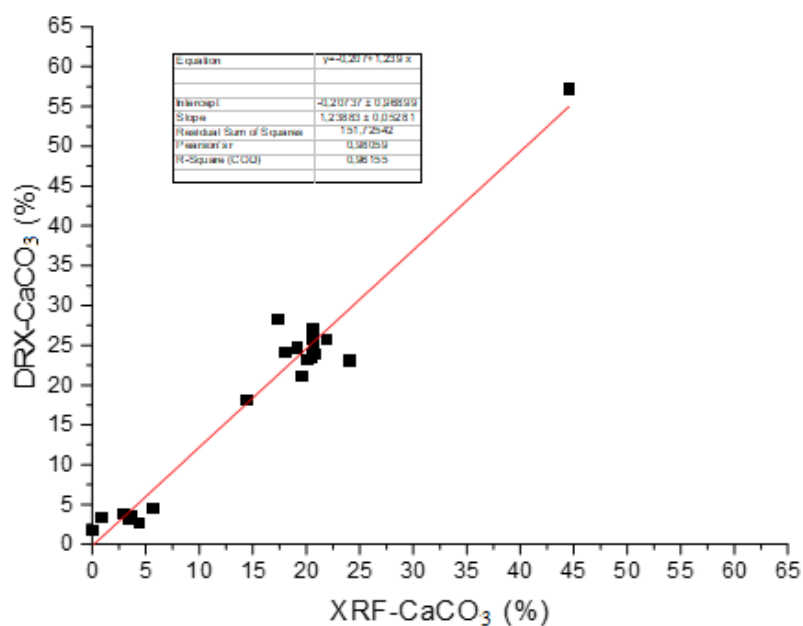
Figure S13. Linear regression model between % $CaCO_3$ obtained by XRF and DRX.

　　　To validate mineralogical $CaCO_3$ composition by XRF and DRX results, investigators applied TGA technique.

　　　Table S2 shows the comparison between percentage $CaCO_3$ by XRF and DRX with percentage $CaCO_3$ by TGA/DCS.

Table S2 Comparative % $CaCO_3$ by DXR, XRF and TGA methods

Sample	$CaCO_3$ % -XRF	$CaCO_3$-DRX	$CaCO_3$-TGA
E60	20,62	24,35	27,06
E60_1	20,59	27,06	26,74
E60_2	20,60	27,3	26,23
E60_3	20,07	23,33	26,01
E60_4	20,51	23,49	25,00
E60_5	19,09	24,8	24,87
E60_6	14,43	18,28	18,60
E69	18,03	23,25	27,11
E69_1	20,55	25,89	30,49
E69_2	20,55	24,03	29,76
E69_3	20,47	23,88	28,27

E69_4	21,87	25,87	28,96
E69_5	19,54	21,3	27,14
E69_6	23,95	23,24	24,79
E70	44,55	57,29	54,45
E80	17,28	28,44	25,83
E90	0	1,81	0,43
E92	2,84	3,88	4,42
E92_1	0,86	3,56	3,51
E92_2	4,31	2,74	4,41
E92_3	3,38	3,17	3,13
E92_4	3,58	3,81	3,83
E92_5	3,33	3,21	2,73
E92_6	5,59	4,62	5,51

It can be appreciated with the slope of linear regression that if XRF technique is used 23,69% carbonates are underestimated (y =0,036+0,763x). If DRX technique is applied, carbonates are underestimated in 3,78% (y = -0,524+0,962).
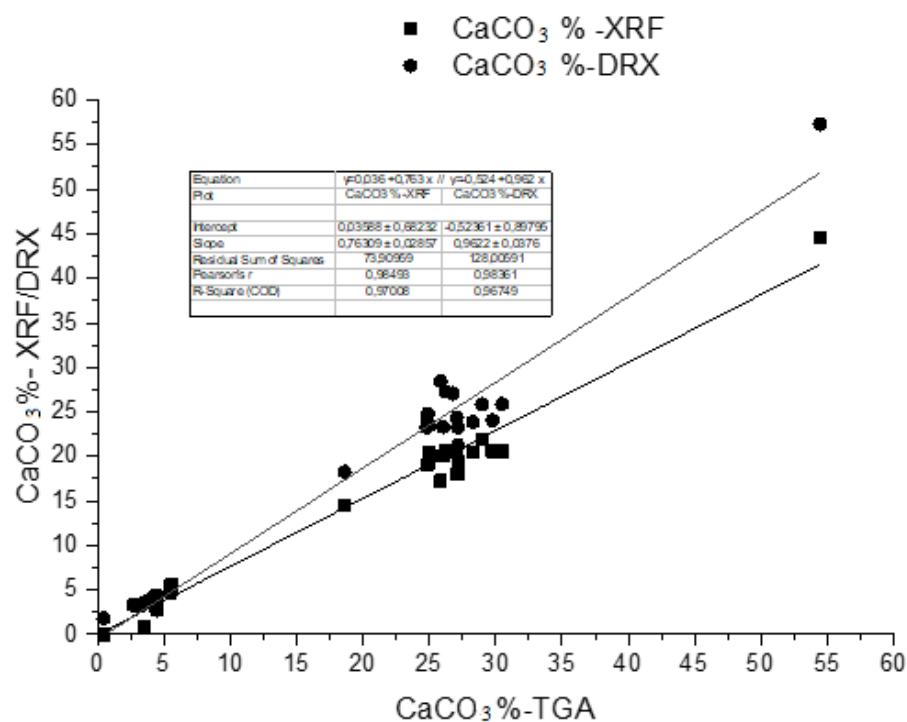

Figure S14. % CaCO$_3$ by TGA vs % CaCO$_3$ by XRF or DRX.