

Elsevier Editorial System(tm) for Radiation Physics and Chemistry
Manuscript Draft

Manuscript Number:

Title: A preliminary study of ceramics from São Paulo II archaeological site by means of TL, EPR, XRD, INAA and OM techniques

Article Type: ISRP-12

Keywords: São Paulo II archaeological site; Pottery; Dating; TL; EPR

Corresponding Author: Dr Sonia Hatsue Tatumi, Ph.D.

Corresponding Author's Institution: Universidade Federal de São Paulo

First Author: Sonia Hatsue Tatumi, Ph.D.

Order of Authors: Sonia Hatsue Tatumi, Ph.D.; Rogerio B Ribeiro, Master; Nilo F Cano, Ph.D.; Casimiro S Munita, Ph.D.; Shiguo Watanabe, Ph.D.; René R Rocca, Master; Eduardo G Neves, Ph.D.; Eduardo K Tamanaha, Master

Abstract: Ceramics from São Paulo II archaeological site were dated by means of thermoluminescence (TL) and the annual doses was determined by U, Th and K concentrations obtained by instrumental neutron activation analysis (INAA). The presence of crystalline and amorphous quartz were studied by X-ray diffraction (XRD) and optical microscopy (OM). Electron paramagnetic resonance (EPR) was used to study the firing temperature using the iron signal (Fe^{3+}) as a firing temperature reference. The age of the samples was found between 895 ± 92 and 1142 ± 100 years and no amorphous quartz was found. The firing temperature was 600-650 °C.

Highlights

- 1) TL Dating of archaeological potteries from Amazon
- 2) Electron paramagnetic resonance (EPR) application for potteries firing temperature analysis.
- 3) U, Th and K concentrations obtained by instrumental neutron activation analysis (INAA)

A preliminary study of ceramics from São Paulo II archaeological site by means of TL, EPR, XRD, INAA and OM techniques

Rogério B. Ribeiro¹, Nilo F. Cano¹, Casimiro S. Munita¹, Shiguelo Watanabe², Sonia H. Tatumi³, René R. Rocca², Eduardo G. Neves⁴, Eduardo K. Tamanaha⁴

¹Instituto de Pesquisas Energéticas e Nucleares IPEN-CNEN/SP, Av. Prof. Lineu Prestes 2242, CEP 05508-000, São Paulo, SP, Brazil

²Instituto de Física, Universidade de São Paulo, Rua do Matão 187, Travessa R CEP 05508-090, São Paulo, SP, Brazil

³Universidade Federal de São Paulo, Av. Alm. Saldanha da Gama, 89, 11030-400, Santos, Brazil

⁴Museu de Arqueologia e Etnologia, Universidade de São Paulo, Av. Prof. Almeida Prado 1466, CEP 05508-900, São Paulo, SP, Brazil

Abstract

Ceramics from São Paulo II archaeological site were dated by means of thermoluminescence (TL) and the annual doses was determined by U, Th and K concentrations obtained by instrumental neutron activation analysis (INAA). The presence of crystalline and amorphous quartz were studied by X-ray diffraction (XRD) and optical microscopy (OM). Electron paramagnetic resonance (EPR) was used to study the firing temperature using the iron signal (Fe^{3+}) as a firing temperature reference. The age of the samples was found between 895 ± 92 and 1142 ± 100 years and no amorphous quartz was found. The firing temperature was 600-650 °C.

Keywords: São Paulo II archaeological site, Pottery, Dating, TL, EPR

1. Introduction

Dating by TL is a particular application of TL dosimetry in which there is a source of constant irradiation (the natural radioactivity of the ceramics), the activity of which can be independently determined.

The duration of irradiation is taken to be the same as the age of the ceramic, and this is proportional to the amount of the TL signal. The duration of underground should be the same as the age of the

ceramics which is proportional to the amount of the TL signal (Aitken, 1985).

TL, OSL and EPR dating of ancient ceramics as based on quartz grain in it contained. The natural radiation that induces the luminescence in quartz grains comes from radioactive ^{40}K , cosmic rays and radionuclides from ^{238}U , ^{232}Th and ^{235}U radioactive series. Actually, ^{235}U series contributes little and not taking into account. These radiation sources determine also the annual dose rate, D_{an}

(Ikeya, 1993; Bartoll and Ikeya, 1997).

1 A pottery is produced heating the clay mold at
2 temperature higher than 500 °C. Heating at such
3 high temperature erase any previous radiation
4 effect, hence if the pottery is buried underground,
5 until it is collected for dating the effect of natural
6 radiation will be accumulated. The accumulate
7 dose (D_{ac}) is measured using additive or
8 regenerate method in the TL technique. The age of
9 the material can be calculated by the D_{ac} divided
10 by the D_{an} (Aitken, 1995; Zimmerman, 1971).

11 The EPR spectroscopy, based on absorption of
12 microwave by an ionic crystal placed in an exter-
13 nal static magnetic field, has two roles as dating
14 technique. One is the usual dating (Ikeya, 1993,
15 Watanabe et al., 2008). The other is find the firing
16 temperature to produce ceramics (Bensimon et al.,
17 1998; Bensimon et al., 1999; Mangueira et al.,
18 2011). The g-factor of EPR signal of some para-
19 magnetic centers can vary with high temperature
20 annealing. Such is the case of the signal asso-
21 ciated with Fe^{3+} and can be used to find the firing
22 temperature to produce ceramics.

23 The São Pablo II archaeological site is located on
24 the left margin of the Solimões River, near the
25 Coari city and 380 km away from the city of
26 Manaus, Brazil (see Fig. 1). A previous study by
27 Tamanaha (2012) has shown that ceramics
28 belongs to a simple phase, Guarita.

29 By investigation of ceramics under different
30 aspects we can find the methodology used in
31 manufacturing ceramics, dynamics of economical
32 nature, cultural and social development of ancient
33 people. Such investigation has contributed to
34 understand not only geographical occupation as
35 well as cultural heritage of ancient people.

36 In many potteries from central Amazon
37 investigated so far, spicules have been found. In

the present case, optical microscopy (OM) and X-
ray diffraction (XRD) were used to verify whether
or not ceramics fragments here investigated
contain spicules.

The TL was used to obtain information about the
chronology of occupation of the site. The way it
was produced and its ceramic firing temperature
were determined by EPR.

2. Experimental

2.1 Sample preparation and chemical treatment

The ceramics to be investigated were sandpapered
to eliminate about 2 mm throughout the ceramic
surface to remove any external effect. In the
following, the samples were crushed and sieved to
retain grain sizes between 0.08 and 0.180 mm.
Thereafter, the powder was subjected to chemical
cleaning with H_2O_2 , HF and HCl procedure that
helps to separate the quartz as well as possible
(Watanabe et al. 2008). The quartz grains after dry
have been subject to magnetic separation using a
Nd magnet to remove magnetic material still
present.

2.2 Analysis of quartz grains

To analyze the presence or not of amorphous
material, namely spicules, an optical microscope
(OM) Bioval mark, model U-1000T in eyepiece
version and capacity of increase between 40 and
1600x has been used.

The XRD measurement was performed using a X-
ray diffractometer model Rigaku equipped with a
source of $Cu-k_{\alpha}$ with wavelength λ of the
monochromatic beam of 1.5418 Å. 100 mg of
samples has been used for each measurement. The
operating voltage was 40 kV and the operating
current of 40 μA . The result of XRD was analyzed
using computer programs and compared with the
standard spectrum of quartz cataloged JCPDS

(Joint Committee Powder Diffraction Standards).

2.3 Electron paramagnetic resonance (EPR)

The ceramics powder resulting from breaking and sieving was subjected to a heat treatment. Initially, 5 samples of ceramics fragments were chosen for heat treatment. Then nine samples were separated in powder form for each sample, these represent about 45 aliquots. Thermal treatment was performed in preheated oven and started with the temperature of 450 °C up to 800 °C. Every sample was thermally treated for 30 min.

Each measurement was made with 70 mg of the sample in powder form, placed inside quartz tube of 4 mm in diameter. The equipment used was the spectrometer Bruker EMX of the Institute of Physics of the University of São Paulo, Brazil. Its cavity with a ER 4102ST operate in X-band and possesses modulation of 100kHz at room temperature. 20 mW of microwave power and modulation of one G have been used.

2.4 Thermoluminescence (TL)

The thermoluminescence measurements were carried out in an automatic TL reader Daybreak model 1100 TL, keeping a heating rate of 4 °C/s in the interval of 50 to 500 °C. For every reading of the sample was used an average of 4 mg. The irradiation of samples has been carried out with gamma radiation source of ⁶⁰Co at the Radiation Technology Center of IPEN/CNEN-SP, Brazil. The doses applied were 0.5; 1.0; 1.5; 2.5; 5.0; 10.0; 20.0 Gy and additive method was used to estimate accumulated dose (D_{ac}). Each glow curve represents an average of five measurements.

The annual dose rate (D_{an}) was calculated from the concentration of U, Th and K of ceramics determined by neutron activation analysis (NAA) at the IEA-R1 Reactor of IPEN/ CENEN-SP, Brazil. Cosmic rays contribution was added in

D_{an} .

3. Results and Discussions

3.1 Optical microscopy and X-ray diffraction

The Fig. 2 shows the microphotograph of the quartz grains obtained with optical microscope. Amorphous material (spicules) has not been observed. As already mentioned, spicules are found in other ceramics material of the Amazon region.

Fig. 3 shows X-ray diffraction pattern of the sample of this work and that of pure standard quartz.

3.2 Electron paramagnetic resonance

Fig. 4 shows the EPR spectrum of analyzed samples, an intense signal around $g=2$ region, which is characteristic of Fe^{3+} in an octahedral site (Warashina et al., 1981; Presciutti et al., 2005; Bensimon et al., 1999; Mangueira et al., 2011). The EPR spectrum too shows another signal at $g=4.3$, typical of Fe^{3+} in an orthorhombic site (Presciutti et al., 2005; Bensimon et al., 1999; Tani et al. 1997), also is observed.

The firing temperature of the ceramics was determined by successive thermal treatment at high temperature where the g -value of Fe^{3+} changes. The Fig 5 shows the behavior of the g factor as function of the temperature for the different potteries samples. All the samples present a variation of the g factor above 500-600 °C. It indicates that the firing temperature determined for the samples analyzed are within of an interval between 600 and 650 °C.

Table 1 shows the values for the firing temperatures for six samples. As can be seen in Table, the values for firing temperatures of ceramic fragments are very close. So the result of the variation factor g indicates that the sample

burned ceramic in this temperature range.

3.3 Thermoluminescence

Fig. 6 shows the TL glow curve of the quartz grains with peaks at 120, 200 and 320-370 °C. The high temperature peak shifts from 370 °C to 320 °C with the dose. Anyway the high temperature peak was used for determination of accumulated dose, D_{ac} by additive method shown in Fig. 7.

An accumulated dose, D_{ac} of about 1,353 Gy was obtained. By neutron activation analysis, concentration of ^{238}U , ^{232}Th and ^{40}K were estimated and these values are listed in Table 2. From these values, D_{an} -values were calculated using Table 4.3 and 4.4 in Ikeya (1993), and ages by deviding D_{ac} by corresponding D_{an} -values, also listed in Table 2.

Using ^{14}C dating, Lima (2006, 2008) has shown that the chronology of the Guarita ceramic phase in Central Amazonian ranged from X to XVI centuries and conform approximately with the present result.

4. Conclusions

Four ceramics sample from São Pablo II archaeological site investigated here do not contain spicules, white many ceramics of from site in the same region have been found containing spicules. Relatively high annual dose rate values were obtained for all four samples. For Brazilian potteries relatively old ages ranging between 900 and 1200 years have been obtained. Therefore the results confirm the archaeological interpretation on the chronology of the occupation of the indian communities that occurred in this region of the central Amazon of Brazil. EPR signal intensity of Fe^{3+} indicates that a heat with a temperature around 600 to 650 °C was used to burn clay to produce ceramics.

Acknowledgement

The authors wish to thank Ms. E. Somessari and Mr. C. Gaia from Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, Brazil, for kindly carrying out the irradiation of the samples and Comissão Nacional de Energia Nuclear, Brazil, by financial support.

Figure Caption

1 Fig. 1 Map of São Paulo II archaeological site

2 **Fig. 2** Photograph of quartz grains found in the
3 sample
4

5 **Fig. 3** X-ray diffractogram of quartz for the ana-
6 lyzed sample and the standard quartz
7

8 **Fig. 4** EPR spectrum for sample CSQSP-49
9

10 **Fig. 5** Variation of the value of g-factor to Fe^{3+}
11 with temperature of heating the experimental
12 sample
13
14

15 **Fig. 6** TL glow curve of the sample to a dose of
16 0.5 to 20 Gy
17

18 **Fig. 7** TL intensity in function of the dose added
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

References

- 1 Aitken, M.J., 1985. Thermoluminescence Dating.
2 Academic Press, London.
- 3 Bartoll, J., Ikeya, M. 1997. Dating of Pottery: a
4 Trial. *Appl. Radiat. Isot.* 48, 981-984.
- 5 Bensimon, Y., Deroide, B., Clavel, S., Zanchetta,
6 J.V., 1998. Electron spin resonance and dila-
7 tometric studies of ancient ceramics applied to
8 the determination of firing temperature. *Jpn. J.*
9 *Appl. Phys.* 37, 4367-4372.
- 10 Bensimon, Y., Deroide, B., Zanchetta, J.V., 1999.
11 Comparison between the electron paramagnet-
12 ic resonance spectra obtained in X- and W-
13 bands on a fired clay: a preliminary study. *J.*
14 *Phys. Chem. Solids* 60, 813-818.
- 15 Lima, H. P., Neves, E.G., Petersen, J.B., 2006.
16 *Arqueologia Suramericana*, 2, 26-52.
- 17 Lima, H. P., 2008. História das Caretas: a tra-
18 dição borda incisa na Amazônia Central.
19 PhD Thesis, Museum of Archaeology and
20 Ethnology, University of São Paulo, São
21 Paulo, Brazil.
- 22 Mangueira, G.M., Toledo, R., Teixeira, S., Franco,
23 R.W.A., 2011. A study of the firing tempera-
24 ture of archeological pottery by X-ray diffrac-
25 tion and electron paramagnetic resonance. *J.*
26 *Phys. Chem. Sol.* 72, 90-96.
- 27 Presciutti, F., Capitani, D., Sgamellotti, A., Bru-
28 netti, B.G., Costantino, F., Viel, S., Segre, A.,
29 2005. Electron Paramagnetic Resonance,
30 Scanning Electron Microscopy with Energy
31 Dispersion X-ray Spectrometry, X-ray Powder
32 Diffraction, and NMR Characterization of
33 Iron-Rich Fired Clays. *J. Phys. Chem. B.* 109,
34 22147-22158.
- 35 Tamanaha, E. K. 2012. Ocupação polícroma
36 no baixo e médio rio Solimões, Estado do
37 Amazonas. Thesis, Museum of Archaeolo-
38 gy and Ethnology, University of São Paulo,
39 São Paulo, Brazil.
- 40 Tani, A., Bartoll, J., Ikeya, M., Komura, K.,
41 Kajiwara, H., Fujimura, S., Kamada, T.,
42 Yokoyama, Y., 1997. ESR Study of Thermal
43 History and Dating of a Stone Tool. *Appl.*
44 *Magn. Reson.*, 13, 561-569.
- 45 Warashina, T., Higashimura, T., Maeda, Y., 1981.
46 Determination of the firing temperature of an-
47 cient pottery by means ESR spectrometry, *Br.*
48 *Mus. Occasional* 19, 117-123.
- 49 Watanabe, S., Farias, T.M.B., Gennari, R.F., Fer-
50 raz, G.M., Kunzli, R., Chubaci, J.F.D., 2008.
51 Chemical process to separate iron oxides par-
52 ticles in pottery sample for EPR dating. *Spec-*
53 *trochimica Acta Part A* 71, 1261-1265.
- 54 Zimmerman, D.W., 1971. Thermoluminescent
55 dating using fine grains from pottery. *Archaeometry* 13, 29-52.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

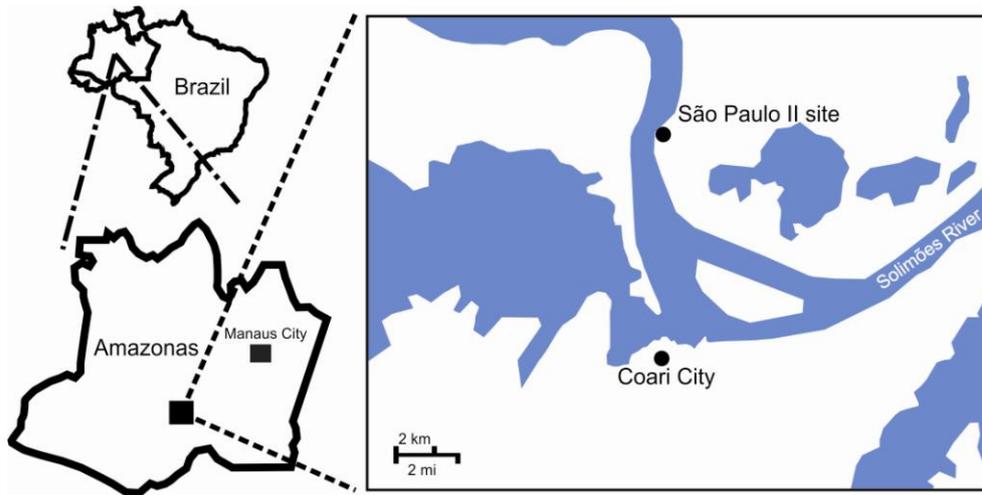


Fig. 1 Map of São Paulo II archaeological site.

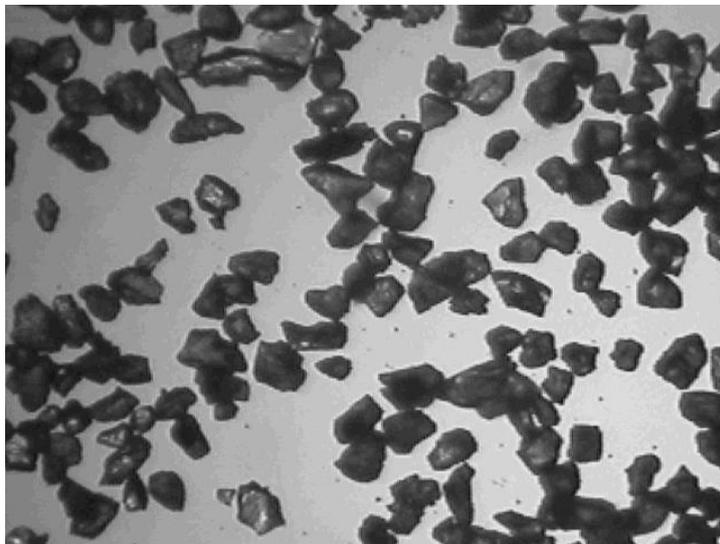


Fig. 2 Photograph of quartz grains found in the sample.

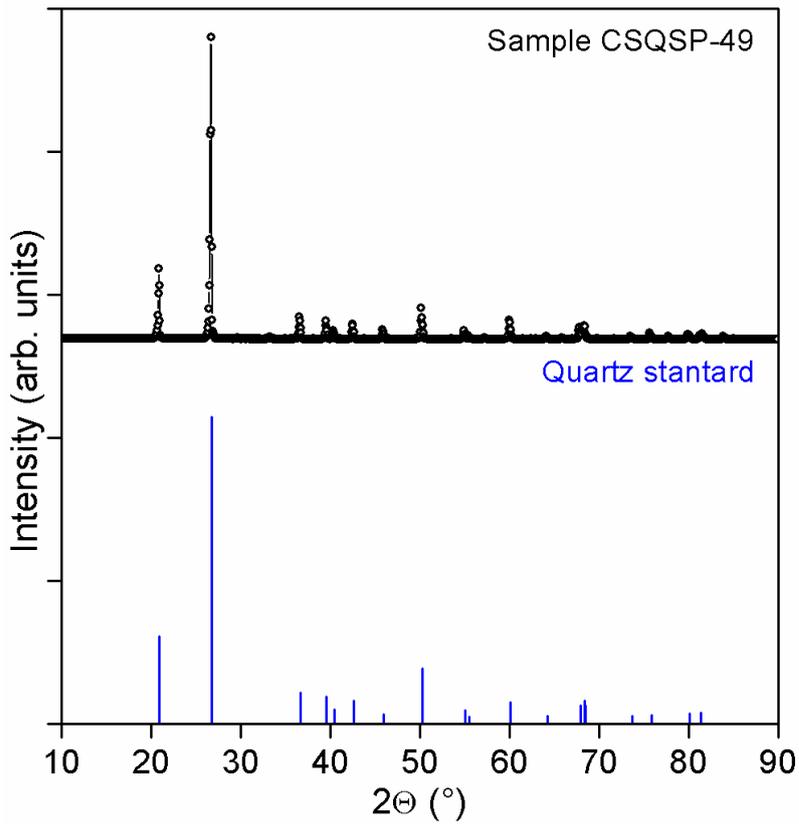


Fig. 3 X-ray diffractogram of quartz for the analyzed sample and the standard quartz.

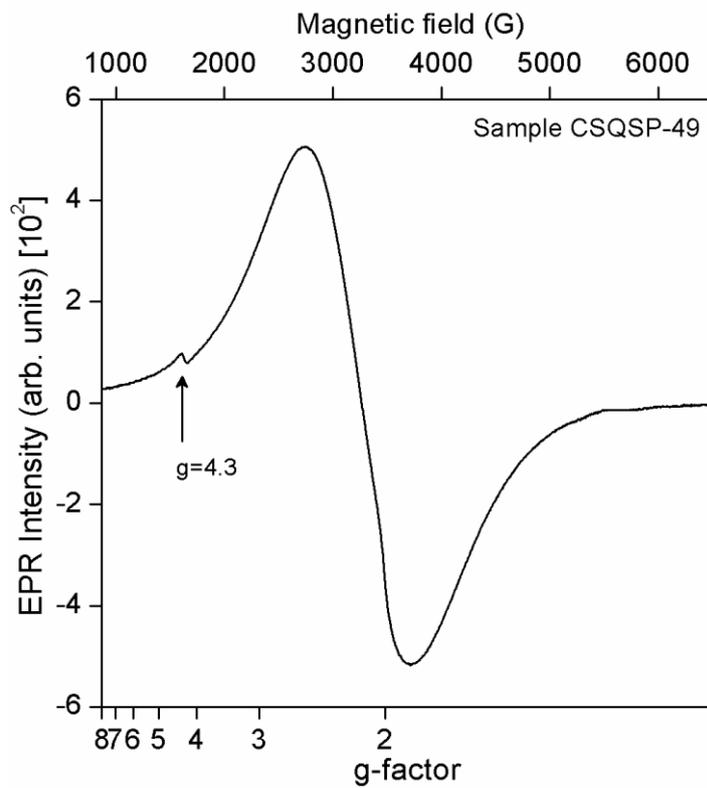


Fig. 4 EPR spectrum for sample CSQSP-49.

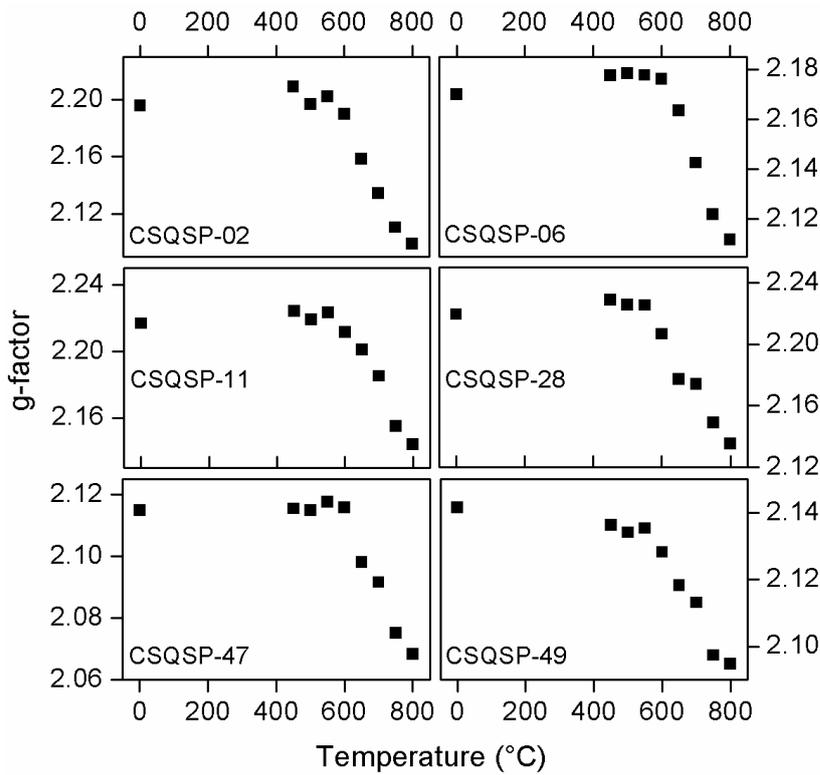


Fig. 5 Variation of the value of g-factor to Fe^{3+} with temperature of heating the experimental sample.

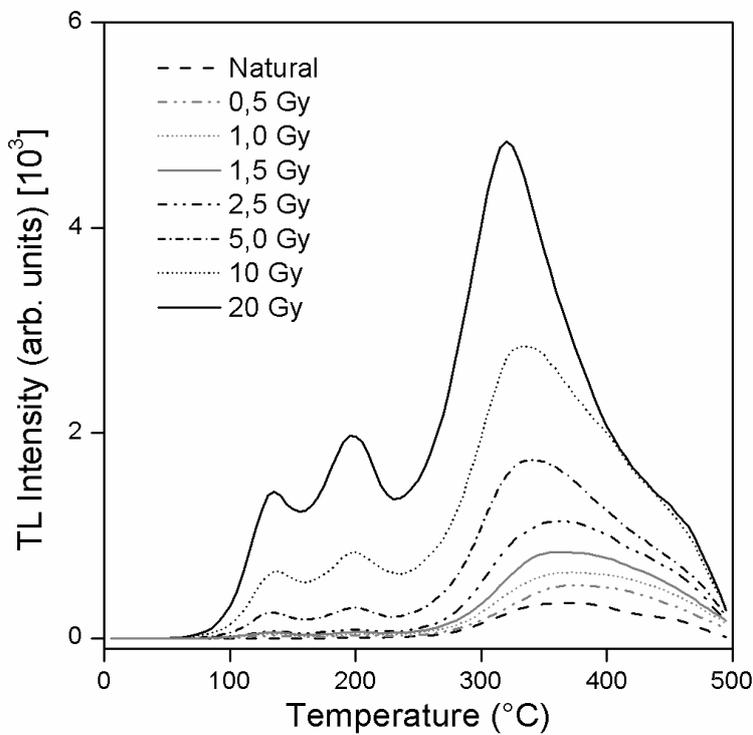


Fig. 6 TL glow curve of the sample to a dose of 0.5 to 20 Gy.

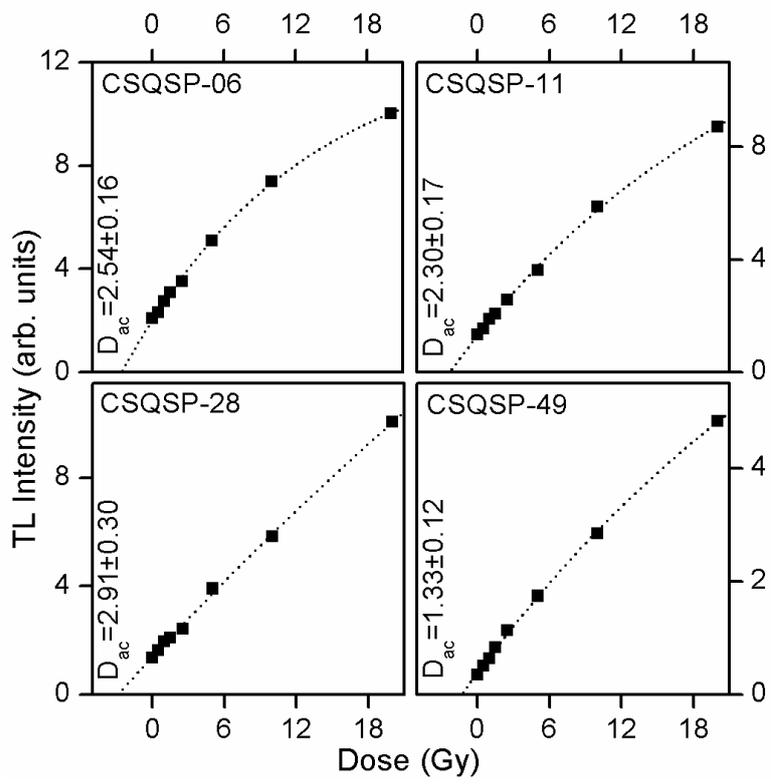


Fig. 7 TL intensity in function of the dose added.

Table 1 Results firing temperature for analyzed samples.

1	2	3
4	5	6
7	8	9
10	11	12
13	14	15
16	17	18
19	20	21
22	23	24
25	26	27
28	29	30
31	32	33
34	35	36
37	38	39
40	41	42
43	44	45
46	47	48
49	50	51
52	53	54
55	56	57
58	59	60
61	62	63
64	65	

Table 2 Accumulated dose, annual dose and age of the fragments of ceramic samples obtained by TL.

24	25	26	27	28	29	30
31	32	33	34	35	36	37
38	39	40	41	42	43	44
45	46	47	48	49	50	51
52	53	54	55	56	57	58
59	60	61	62	63	64	65
66	67	68	69	70	71	72
73	74	75	76	77	78	79
80	81	82	83	84	85	86
87	88	89	90	91	92	93
94	95	96	97	98	99	100
101	102	103	104	105	106	107
108	109	110	111	112	113	114
115	116	117	118	119	120	121
122	123	124	125	126	127	128
129	130	131	132	133	134	135
136	137	138	139	140	141	142
143	144	145	146	147	148	149
150	151	152	153	154	155	156
157	158	159	160	161	162	163
164	165	166	167	168	169	170
171	172	173	174	175	176	177
178	179	180	181	182	183	184
185	186	187	188	189	190	191
192	193	194	195	196	197	198
199	200	201	202	203	204	205
206	207	208	209	210	211	212
213	214	215	216	217	218	219
220	221	222	223	224	225	226
227	228	229	230	231	232	233
234	235	236	237	238	239	240
241	242	243	244	245	246	247
248	249	250	251	252	253	254
255	256	257	258	259	260	261
262	263	264	265	266	267	268
269	270	271	272	273	274	275
276	277	278	279	280	281	282
283	284	285	286	287	288	289
290	291	292	293	294	295	296
297	298	299	300	301	302	303
304	305	306	307	308	309	310
311	312	313	314	315	316	317
318	319	320	321	322	323	324
325	326	327	328	329	330	331
332	333	334	335	336	337	338
339	340	341	342	343	344	345
346	347	348	349	350	351	352
353	354	355	356	357	358	359
360	361	362	363	364	365	366
367	368	369	370	371	372	373
374	375	376	377	378	379	380
381	382	383	384	385	386	387
388	389	390	391	392	393	394
395	396	397	398	399	400	401
402	403	404	405	406	407	408
409	410	411	412	413	414	415
416	417	418	419	420	421	422
423	424	425	426	427	428	429
430	431	432	433	434	435	436
437	438	439	440	441	442	443
444	445	446	447	448	449	450
451	452	453	454	455	456	457
458	459	460	461	462	463	464
465	466	467	468	469	470	471
472	473	474	475	476	477	478
479	480	481	482	483	484	485
486	487	488	489	490	491	492
493	494	495	496	497	498	499
500	501	502	503	504	505	506
507	508	509	510	511	512	513
514	515	516	517	518	519	520
521	522	523	524	525	526	527
528	529	530	531	532	533	534
535	536	537	538	539	540	541
542	543	544	545	546	547	548
549	550	551	552	553	554	555
556	557	558	559	560	561	562
563	564	565	566	567	568	569
570	571	572	573	574	575	576
577	578	579	580	581	582	583
584	585	586	587	588	589	590
591	592	593	594	595	596	597
598	599	600	601	602	603	604
605	606	607	608	609	610	611
612	613	614	615	616	617	618
619	620	621	622	623	624	625
626	627	628	629	630	631	632
633	634	635	636	637	638	639
640	641	642	643	644	645	646
647	648	649	650	651	652	653
654	655	656	657	658	659	660
661	662	663	664	665	666	667
668	669	670	671	672	673	674
675	676	677	678	679	680	681
682	683	684	685	686	687	688
689	690	691	692	693	694	695
696	697	698	699	700	701	702
703	704	705	706	707	708	709
710	711	712	713	714	715	716
717	718	719	720	721	722	723
724	725	726	727	728	729	730
731	732	733	734	735	736	737
738	739	740	741	742	743	744
745	746	747	748	749	750	751
752	753	754	755	756	757	758
759	760	761	762	763	764	765
766	767	768	769	770	771	772
773	774	775	776	777	778	779
780	781	782	783	784	785	786
787	788	789	790	791	792	793
794	795	796	797	798	799	800
801	802	803	804	805	806	807
808	809	810	811	812	813	814
815	816	817	818	819	820	821
822	823	824	825	826	827	828
829	830	831	832	833	834	835
836	837	838	839	840	841	842
843	844	845	846	847	848	849
850	851	852	853	854	855	856
857	858	859	860	861	862	863
864	865	866	867	868	869	870
871	872	873	874	875	876	877
878	879	880	881	882	883	884
885	886	887	888	889	890	891
892	893	894	895	896	897	898
899	900	901	902	903	904	905
906	907	908	909	910	911	912
913	914	915	916	917	918	919
920	921	922	923	924	925	926
927	928	929	930	931	932	933
934	935	936	937	938	939	940
941	942	943	944	945	946	947
948	949	950	951	952	953	954
955	956	957	958	959	960	961
962	963	964	965	966	967	968
969	970	971	972	973	974	975
976	977	978	979	980	981	982
983	984	985	986	987	988	989
990	991	992	993	994	995	996
997	998	999	1000			