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THERMOGRAVIMETRIC STUDY OF DIATOMITES

S. Mendioroz, M. J. Belzunce and *J. A. Pajares**

INSTITUTO DE CATÁLISIS Y PETROLEOQUÍMICA, CSIC,
SERRANO 119, 28006–MADRID, SPAIN

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The thermal curves of diatomites (kieselguhrs) in air display different profiles, depending on the type and quantity of impurities (carbonates, clays, etc.) present. TG and DTG runs can be used for a quick diagnosis of quality, but also give a nearly quantitative picture of the silica content of these minerals.

Diatomites (or kieselguhrs) are mineral deposits of diatomaceous algae, those commercially exploited being restricted to a relatively modern age, starting from the Miocene. Older deposits have suffered tectonic processes, bringing about modifications of the texture and crystalline phase of the mineral. Amorphous silica, a constituent of the diatom frustulae, is the main component of diatomite, although variable quantities of other materials (metal oxides, clays, salts (mainly carbonates) and organic matter) may also be present. Chemical precipitation and atmospheric contact, together with the prevailing environmental conditions, are determinant factors in the nature and importance of the impurity content of a deposit.

The diatomite resources in the world will be more than sufficient for many years to come if no new applications are developed. The possibility of utilization of a specific deposit depends on the quality of the mineral involved, this requiring adequate characterization, for which the corresponding techniques must be developed.

The present work reports on a thermogravimetric study of twelve samples of different diatomite deposits from S and SE Spain. Thermogravimetry proved to be an efficient and rapid method for mineral diagnosis, the shapes of the TG curves giving the carbonate and silica contents of the diatomite samples almost quantitatively.

* To whom all correspondence should be addressed.

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Experimental

Materials

Samples of minerals were chosen from among the more representative ones of the four geographical zones where diatomite deposits are found in Spain [1, 2]: Sevilla (one sample, Lebrija) Cordoba-Jaén (two samples, Calatrava and Andujar), Almeria (one sample) and Albacete-Murcia (eight samples). Details on the occurrence are given elsewhere [3]. Chemical analyses and textural parameters are listed in Table 1. Details on the experimentation and IR spectra, X-ray diffraction patterns and SEM micrographs are to be found in [3–5].

The chemical analyses revealed clear differences between minerals with (1) a high silica content ($\simeq 80$ wt% SiO_2, Elche, Hellin CS, MC–CAR, Lebrija); (2) a low silica content (Almeria, RB–3, RB–4); and (3) silica contents in the range 57–75 wt% and fair amounts of water, carbonates and other impurities. The textural parameters are typical of those found in kieselguhr [6, 7].

Equipment

TG analyses were performed in a Perkin–Elmer TGS–2 thermobalance, with a System 7/4 temperature controller, a PE 3600 data station and an X–Y recorder; the sensitivity was 0.2 µg. The experimental working conditions were atmospheric air and a heating rate of 10 deg/min in the range RT–900°. The sample weight varied between 20 and 50 mg. Previous storage took place in a desiccator at constant humidity ($CaCl_2$).

Results and discussion

TG and DTG profiles of the twelve samples are displayed in Fig. 1. Some chemical and mineralogical characteristics of the samples can be inferred from them, especially when working with materials from the same geological basin, in spite of the apparent temperature and weight loss differences.

In general, three steps can be detected in the thermal curves of the diatomites, although other minor peaks may also be present. The first main step, produced at temperatures between 25 and $100° \pm 10°$, is related with mechanically trapped and/or physisorbed water, its quantity depending on the particle size and surface area of the samples, as well as on the relative humidity to which they had been exposed prior to their analysis. This peak does not depend on the chemical nature of the sample, but it is related only with morphological and textural parameters.

The second step, due to structural water loss, appears between 100 and

Table 1 Chemical analysis (%) and textural parameters of diatomites

Sample	Chemical composition, %								Total weight loss, %	S_{BET}, $m^2\ g^{-1}$	d, μm	V_p, cm^3/g	ϱ_{ap}, g/cm^3
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O					
Hellin CS	84.46	0.40	0.07	0.12	0.65	0.12	1.80	0.60	10.56	7.4	8.4	1.87	0.47
Elche	82.04	0.81	0.75	0.05	0.86	0.32	3.14	0.21	8.75	25.4	15	2.80	0.405
MC–CAR	82.56	0.14	0.06	0.06	0.44	0.09	0.14	0.07	11.26	15	4.2	1.27	0.57
MC–40	75.74	0.75	0.52	0.02	1.52	0.30	0.80	0.62	14.51	9.6	12	1.35	0.58
MC–1	69.12	0.69	0.30	0.08	3.23	1.16	2.28	1.58	16.4	12.0	10	1.29	0.64
MC–10	68.81	0.18	0.14	0.06	2.98	0.13	3.24	1.74	14.28	13.2	13	1.28	0.61
RB–4	54.82	1.12	0.36	0.07	11.49	0.53	0.89	0.19	22.09	8.9	4.1	1.28	0.67
RB–3	21.58	0.52	0.30	0.06	18.22*	0.88	0.75	0.09	35.19	5.2	8	1.08	0.83
Andujar	65.86	8.86	1.97	0.45	10.28	1.14	0.24	1.05	15.16	19.0	11.8	1.46	0.45
Calatrava	56.92	1.21	1.24	0.10	17.54	0.27	2.64	0.43	19.41	21.2	18.6	1.45	0.73
Lebrija	79.26	2.09	0.99	0.11	2.30	1.28	1.83	2.67	13.22	10.5	7.8	1.40	0.64
Almeria	3.64	3.02	0.69	0.17	47.54**	0.44	1.13	1.38	39.99	11.1	5.2	0.65	1.11

* $CaCO_3$, 32.52%.
** $CaCO_3$, 84.91%.

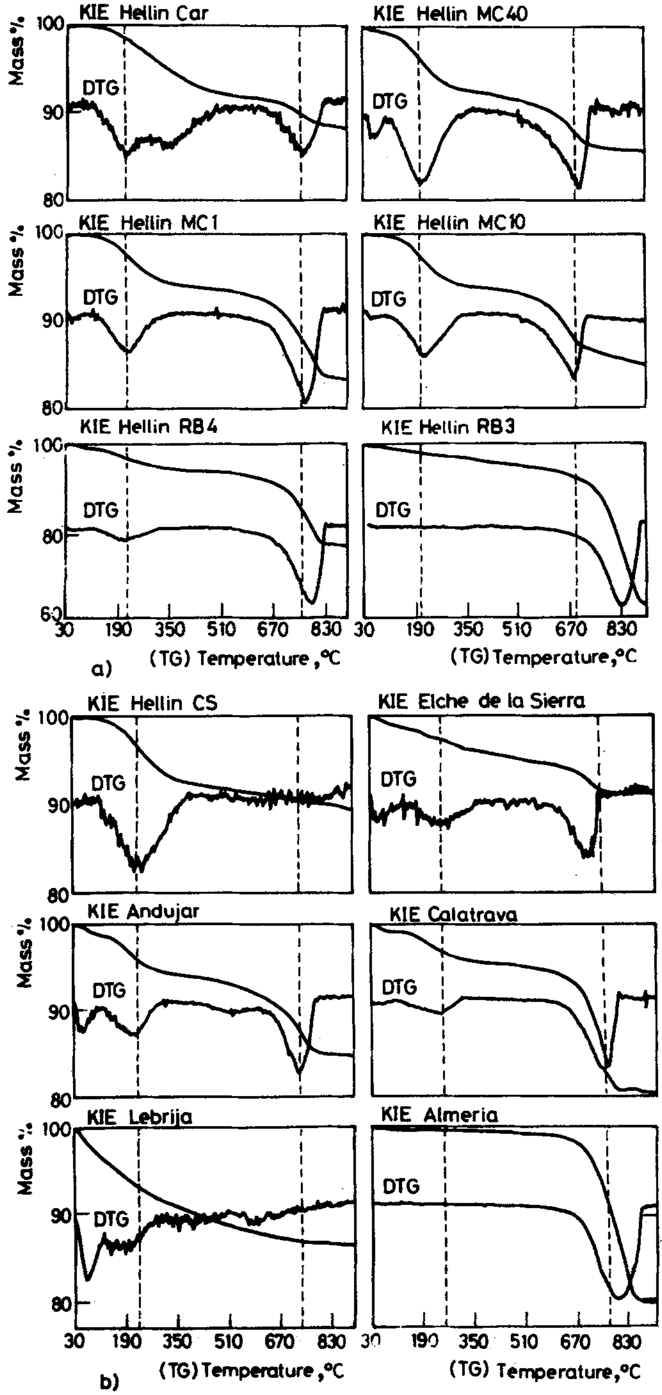

Fig. 1 TG and DTG curves of diatomites. Experimental conditions: Air ($p \simeq 700$ mm Hg), heating rate 10 deg/min

350° ± 20°, and is mainly related with the nature of the opaline phase. It is typical of Opal–A, the main component of diatomite, a highly disordered, nearly amorphous, natural hydrous silica [8], with an X-ray diffuse band centered around 4.1 Å. It is known [9, 10] that the nature of this structural water depends upon the nature of the silica in which it resides: Opal–A, Opal–C, Opal–CT, granular microcrystalline quartz, one of the several varieties of fibrous quartz, or well-crystallized α-quartz. Knauth and Epstein [11–13] have studied the weight losses of diatomites by using differential isotopic exchange, and have reached some important conclusions about the nature of the water in the various forms of hydrous silica.

The third step, at around 750° ± 80°, corresponds to the decomposition of alkali metal and alkaline earth metal carbonates [14], always present in diatomite [15]. Their nature and concentration determine the differences in decomposition temperature of the samples: lower for alkaline metal, higher for alkaline earth metal elements.

Between those last two steps, one or more additional losses are sometimes detected. The lower-temperature weight loss (350°) corresponds to the evolution/decomposition of organic matter, a usual component of diatomite [15], and the higher one to the loss of constitutional water from clay minerals that can sometimes impurify the material. The combination of two or more of these processes may give rise to shifts in the standard profiles of the thermal curves.

With the exception of the Almeria sample, all the samples lose their structural water at the same temperature (DTG maximum at around 190°), denoting a similar evolution of the opaline phase.

In spite of the apparent differences in the thermal curves, a clear correlation is seen among the samples from different beds of El Cenajo basin (MC–CAR, MC–40, MC–10, MC–1, RB–4 and RB–3). This deposit, as indeed all those from Albacete, is lacustrian in origin, and diatomite occurs associated with lime and limestone beds that diminish the silica content of the deposit [15]. The typical three steps referred to above are clearly apparent in this series, indicating carbonates as the sole impurity of these materials. Only MC–CAR, from the more external layer of the deposit, presents an additional weight loss at around 350°, corresponding to organic matter. The importance of the third step is therefore strictly related with the carbonate content of a sample (compare RB–3, 18.22% CaO, and RB–4, 11.49% CaO); it roughly counterbalances the semond step (structural water of silica as A–Opal), and can be used as an index of the purity of a sample.

Slight differences can be seen in the TG of the Hellin and Elche samples, also from Albacete, with an almost undetectable high-temperature weight loss for the former (the purest of all studied samples (Table 1)) and a shift of the second step to higher temperatures (190° →260°) for Elche, due to the influence of alkaline feldspars, whose first structural water is evolved at around this temperature.

The main characteristic of Jaen diatomites is that they contain clays, as the corresponding thermal curves show. In this geological zone, diatomite occurs in aloctone beds of great structural complexity in association with Miocenic marls and marly limestone [15]. The Andujar and Calatrava samples present a similar profile, the second step being more developed in the former, as corresponds to a higher content of clay, and the third one, due to calcium carbonate, in the latter. The Andujar sample also presents a fourth peak, at around 510°, corresponding to a second constitutional water loss from the smectite-type clays [16] present. The Lebrija sample exhibits a profile indicative of a high content of palygorskite-type clays, as well as a lack of carbonates decomposing at around 750°, in accordance with its lacustrian Pliocenic origin, with an upper bed of sepiolite-palygorskite material [17]. The well-known water uptake (3.48%), the faint deflection of the structural water loss peak toward higher temperatures, and a new loss at around 400°, confirm the palygorskite occurrence [18].

Finally, the Almeria sample presents only the step corresponding to alkaline earth metal carbonate decomposition with CO_2 evolution, without further weight loss up to 650°. The calcium carbonate content of the sample is 84.9% (Table 1). According to Calvo Sorando [15], the deposit is formed by claystone sediments (mainly palygorskite) and calcite, with a small proportion of diatomite between beds. In this sample, only carbonate has been detected, and it can therefore hardly be regarded as a diatomite.

From all these results, the possibility emerges of quickly obtain relevant information on the purity and nature of diatomites from thermal analysis (TG and

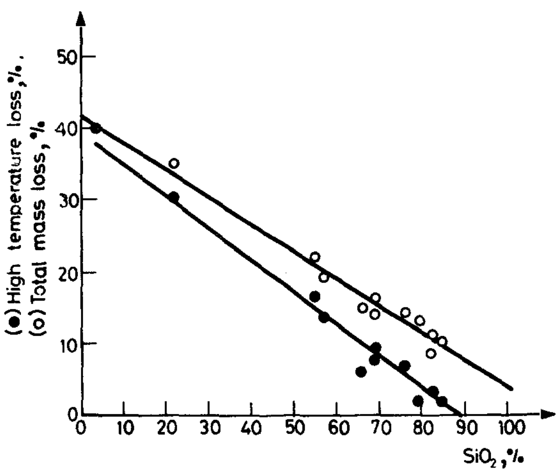

Fig. 2 I. Total weight loss *vs.* silica content of diatomites. II. High-temperature loss *vs.* silica content of diatomites

DTG) experiments. In fact, a plot of the total weight loss against the percentage of silica for all twelve samples (Fig. 2) gives a straight line (curve I), with a correlation coefficient higher than 0.99. The corresponding representation *vs.* the high-temperature loss (CO_2, curve II) reveals an important departure from linearity for the Lebrija and Andujar samples, denoting an impurity other than carbonate, as mentioned above.

Undoubtedly, this plot (slope −0.38, ordinate 42) can be used as a rough guide for a quick analysis of a diatomite mineral, its reliability increasing with decreasing concentration of impurities different from alkaline metal and alkaline earth metal carbonates.

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Zusammenfassung — In Abhängigkeit von Art und Menge der Verunreinigungen (Karbonate, Tonerde usw.) weisen die thermischen Kurven von Diatomiten (Kieselguhr) in Luft unterschiedlichen Verlauf auf. Einfache TG- und DTG-Untersuchungen können als Schnelldiagnose zur Bestimmung der Qualität benutzt werden und geben ausserdem noch ein nahezu quantitatives Bild über den Silikatgehalt dieser Mineralien.

Резюме — Термические кривые диатомитов (кизельгуров) в атмосфере воздуха имели различный профиль, в зависимости от типа и количества примеси (карбонаты, глины и т. п.). Кривые ТГ и ДТГ могут быть использованы не только для их качественной характеристики, но также и для почти количественного определения содержания в них двуокиси кремния.