AN APPARATUS FOR SIMULTANEOUS THERMAL ANALYSIS AND ITS APPLICATIONS IN GEOLOGICAL RESEARCH

EQUIPO PARA EL ANALISIS TERMICO SIMULTANEO Y SU USO EN LAS INVESTIGACIONES GEOLOGICAS

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ABSTRACT: Combination of a home-made thermoanalytical device (Derevatograph, MOM) and a quadrupole mass spectrometer (QMS-D, ATOMKI) is presented, and the simultaneous thermoanalytical method (DTA, DTG, TG, QMS-EGA) has been successfully applied in many fields of mineralogy, petrology, geochemistry and chemostratigraphy.

In Hungary, positive experience has been obtained in the following fields:

- Determination of rare mineral in the Carpathián Basin.
- Diagenetic and hydrothermal processes and facies were characterized by distinguished mineral associations in Hungary and Cuba.
- Geological dating by investigation of sporadic finds (bones) of Neogene vertebrates.

RESUMEN: Se presenta la combinación de un termoanalítico (Derivatograph, MOM) de producción nacional y un espectrómetro cuádruple de masa (QMS-D, ATOMKI), el método termoanalítico simultáneo (DTA, DTG, TG, QMS-EGA) ha sido aplicado exitosamente en muchos campos de la mineralogía, petrología, geoquímica y quimioestratigrafía.

En Hungría se han obtenido experiencias positivas en los siguientes campos:

- Determinación de minerales raros en la cuenca de los Cárpatos.
- Fueron caracterizadas facies y procesos diagenéticos e hidrotermales a través de la distinción de asociaciones minerales de Hungría y Cuba.

INTRODUCTION

The most important informations on various evolved gas analytic methods, such as mass spectrometry, gas chromatography, infra-red absorption, selective sorption and thermogas titrimetry will be found in the books and in well-know scientific journals and monographs. The proceeding of the ICTA and ESTA provide an up-to-date picture of the stage of development of MS and GC-MS coupling system and their applications [e.g. Bracewell et Robertson, 1980; Fripiat, 1982; Morgan, 1977; Müller-Vonmoos et Müller, 1974; Paulik et Paulik, 1981; Székely *et al.*, 1980; Warne *et al.*, 1985].

The new method was used paralelly with thermogas titrimetry (TGT) and IR, GC, X-ray analyses to determine composition of the inorganic and organic compounds, minerals, rocks, building and raw materials, and has been successfully applied in many fields of chemistry and geochemistry [Dévai *et al.*, 1984; Kozák *et al.*, 1985; Szöór *et al.*, 1984; Sözot et Bohátka, 1985; Zöor et Balázs, 1988].

A few examples demonstrate that simultaneous technique is very helpful and it is a basic method for wide area of experience.

Instrument and method

A home-made quadrupole mass spectrometer [Berecz et al., 1983] has been coupled to the Derivatograph and got a versatile instrument promising the possibility of a fast, sensitive evolved gas analysis (Figure 1).

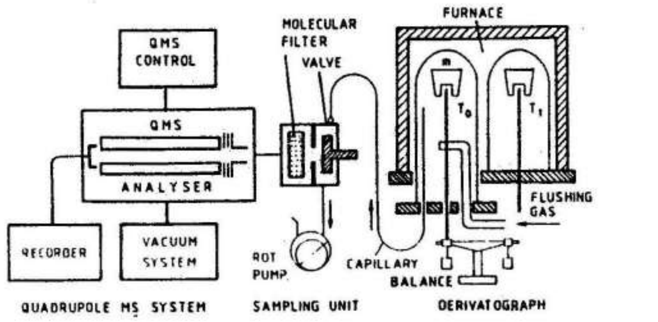

FIGURE 1. Schematic drawing of the Derivatograph (MOM) and QMS-D (ATOMKI) system.

The quadrupole mass spectrometer has a mass range of 1-300 a.m.u. and a sensitivity of 4 x 10^{-4} A/mbar with Faraday cup. It is mounted on a bakeable high vacuum system consisting of a liquid nitrogen cooled refrigerator, water cooled oil trap and oil diffusion pump. Ultimate pressure is less that 1 x 10^{-8} mbar without baking. Gases are pumped from the reaction chamber through a 1,2 m long capillary and a small portion of the sample is introduced into the quadrupole via a molecular filter at the low-pressure end of the capillary. The tip of capillary is 2 cm below the sample holder. The coupling unit can be heated up to 200 ^{0}C, its gas consumption is about 0,5 cm^3/s , response time is 50 ms but this latter is not exploited because of the large volume of the reaction chamber (~ 50 cm^3).

The response time of the whole coupled system is 20 s at 3 cm /s air flow rate. This is satisfactory as the fastest heating program of the Derivatograph is 20 ^{0}C/min . Sensitivity: during the thermoanalysis of 1 mg $Ca(COO)_2$ H_2O the signal at the output of the quadrupole is 50 times higher than the noise amplitude.

The volatile components are identified on the basis of the complete mass-spectra, while the changes in each component of given mass are monitored as a function of temperature with the aid of a peak selector.

The measurements were performed under following conditions: temperature range 1 000 ^{0}C; rate of heating: 10 ^{0}C/min in helium/air current; sample holder: platinum/ceramic crucibles.

The interpretation of calcium oxalate monohydrate (whewellite) and example of our first investigations (Figure 2).

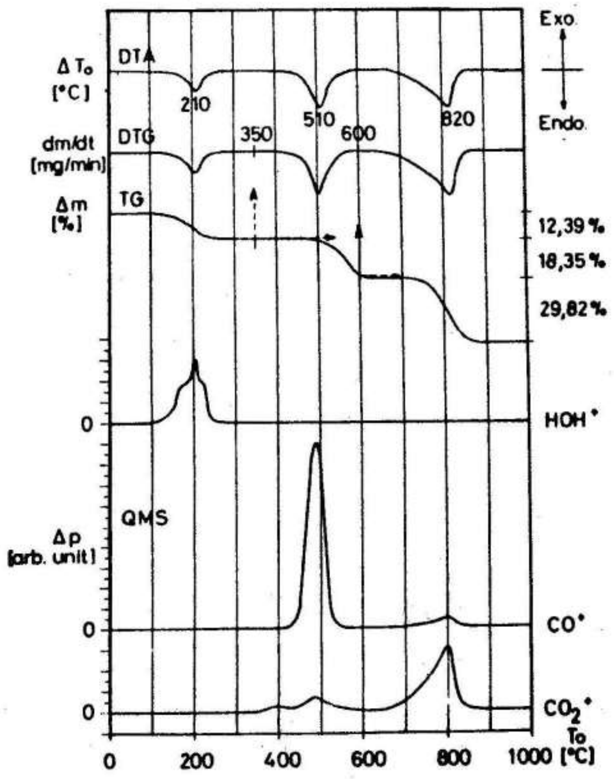

FIGURE 2. The thermal decomposition of whewellite.

The decomposition processes take place as follow in helium atmosphere.

$Ca(COO)_2 . H_2O = Ca(COO)_2 + H_2O$ 210 ^{0}C (1)

$Ca(COO) = CaCO_3 + CO$ 510 ^{0}C (2)

$2 CO = CO_2 + C$

$CaCO_3 = CaO + CO_2$ 820 ^{0}C (3)

$CaCO_3 + C = CaO + 2 CO$

The processes are different in air atmosphere

Results and discussion

The examples reported in this paper demonstrate that simultaneous technique is a very helpful means in the characterization of geological materials.

Mellite, hydrate aluminium mellate, Al_2 [$C_{12}O_{12}$]. 18 or 16 (?) H_2O is a very rare mineral, it is unique in the Carpatic Basin (Csordakút, Hungary). The crystal water content of mellite was controversial up to the present. The Figure 3, shows the loss of water in the first endothermic process is 39,73 % ~16 moles in the formula (Szőor et Bohátka, 1985].

A Lower Pannonian (Miocene) gravel complex is cemented by marcasite deposited by low temperature hydrothermal activity (Viczián et al., 1986]. In this locality the light yellow incrustation on the weathered rock surfaces were hydrous iron sulphate minerals. The X-ray diffraction indicated the minerals as copiapite, (Fe^{2+}, Mg)Fe_4^{3+} [$(OH)(SO_4)_3$ .20 H_2O and rhomboclase, Fe^{3+} H[SO_4] . 4 H_2O The combined thermoanalytical investigations showed H_2O and SO_2 as main components, minor amounts of S and CO_2 indicated impurities in the evolved gases (Figure 4).

The porcentages of the hydrous sulphate minerals are copiapite: 54 per cent, rhomboclase: 23 per cent as computed considering the weight loss of H_2O and SO_3 from the total sample. The remaining 23 per cent is mainly amorphous SiO_2.

This method was used to determine silicate, carbonate, hydroxide mineral paragenesis of ultramaffic rocks (peridotite, serpentinite). According to the water and carbon dioxide detected to antigorite, chrysotile, brucite and magnesito-calcite were identified (Figure 5).

The mass spectrometry combined with Derivatograph can reveal the presence of various carbonates, sulphated, clay minerals in raw and building materials. Figure 6 shows to typical examples.

At the foreground of North Borsod Karst, Hungary, there are some shallow boreholes, which have organic material bearing layers in the Upper Pannonian ingression lagoon sediments. Two characteristic diagenetic processes and facies were distinguished by DTA, DTG, TG, QMS-EGA, GC, IR and Rock Eval pyrolysis methods [Szőor *et al.*, 1986]. In the siderite facies, the organic material was desintegrated under oxidative circumstances, while in the case of calcite and gel pyrite facies, typical aliphatic protobitumens accumulated in a reductive environment (Figure 7).

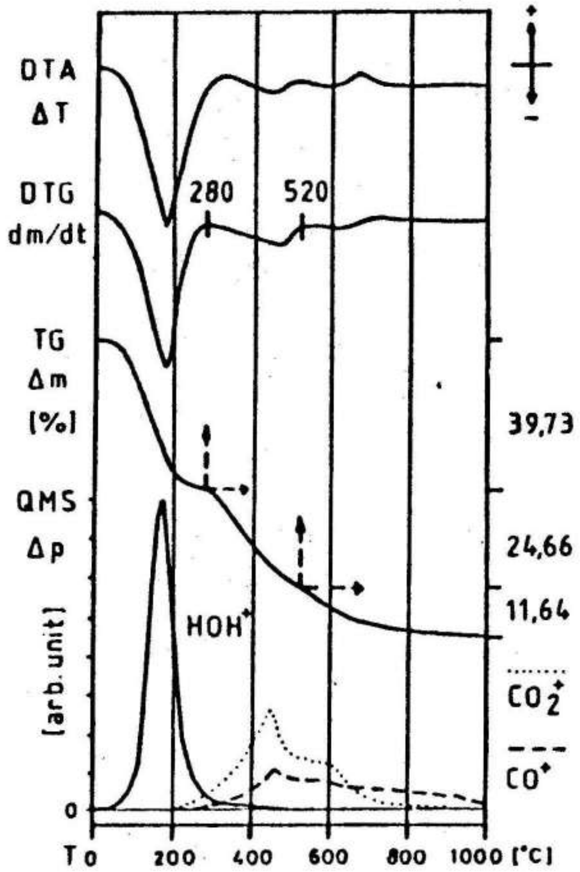

FIGURE 3. The thermal decomposition of mellite.

A new geochronological method has been developed by one of the authors [Szőor, 1982 a, b; Szőor *et al.*, 1987]. The evaluation of the DTA, DTG, TG curves of Quaternary vertebrate fossil materials produced characteristic parameters closely related to geological age. Using this statement as a means for dating carried out a chronostratigraphic evaluation.

In this paper we demonstrate the mass spectrometric thermal analysis which provided the required information to explain the difference in the composition of fossil bones by measuring the evolved gases.

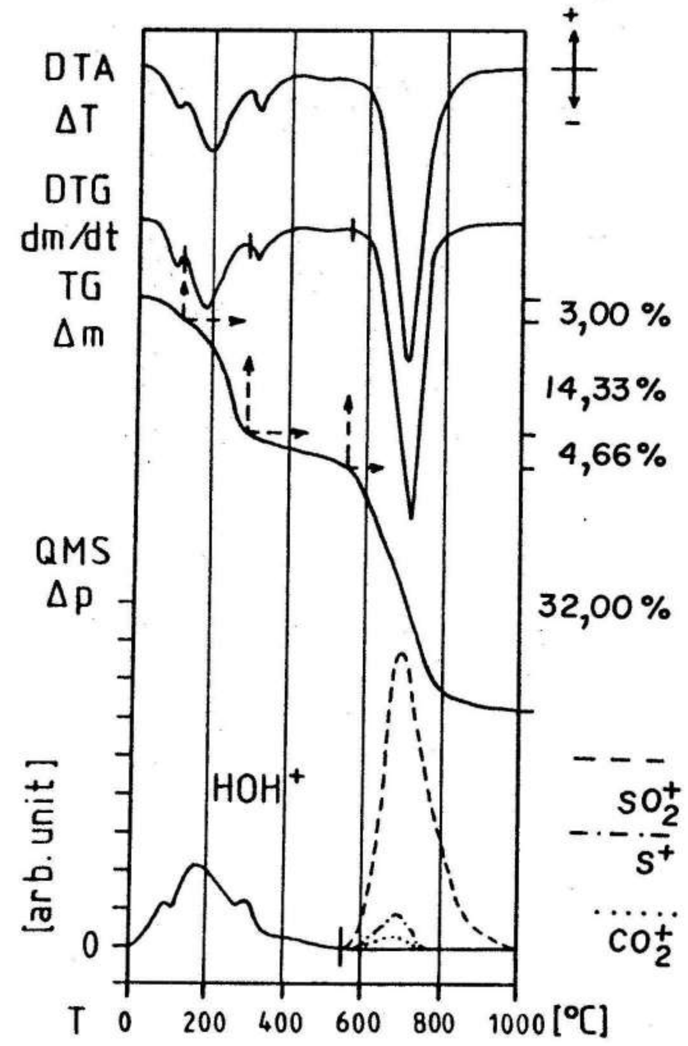

FIGURE 4. The Thermal decomposition of mixture copiapite and rhomboclase.

In the course of our work this chronological well-defined sporadic find was evaluated. The first data is 20 100 years, the other one is 100 000 years. Figure 8, shows the results of examinations. Water as basic constituent was released up to 220 ^{0}C from the organic and inorganic structures (A process). In this range carbon dioxide relates to the beginning of the decomposition of fossile collagen. The main process B takes place between 220 and 600 ^{0}C . The quantity and MS-pattern of organic gas components are different in samples of different ages. The carbonate of apatite and calcite secondarily built into the structure dissociated in the range of 600 - 1 000 ^{0}C (C process).

In the future will be completed to reveal the regularities of collagen with check by GC-MS analyses.

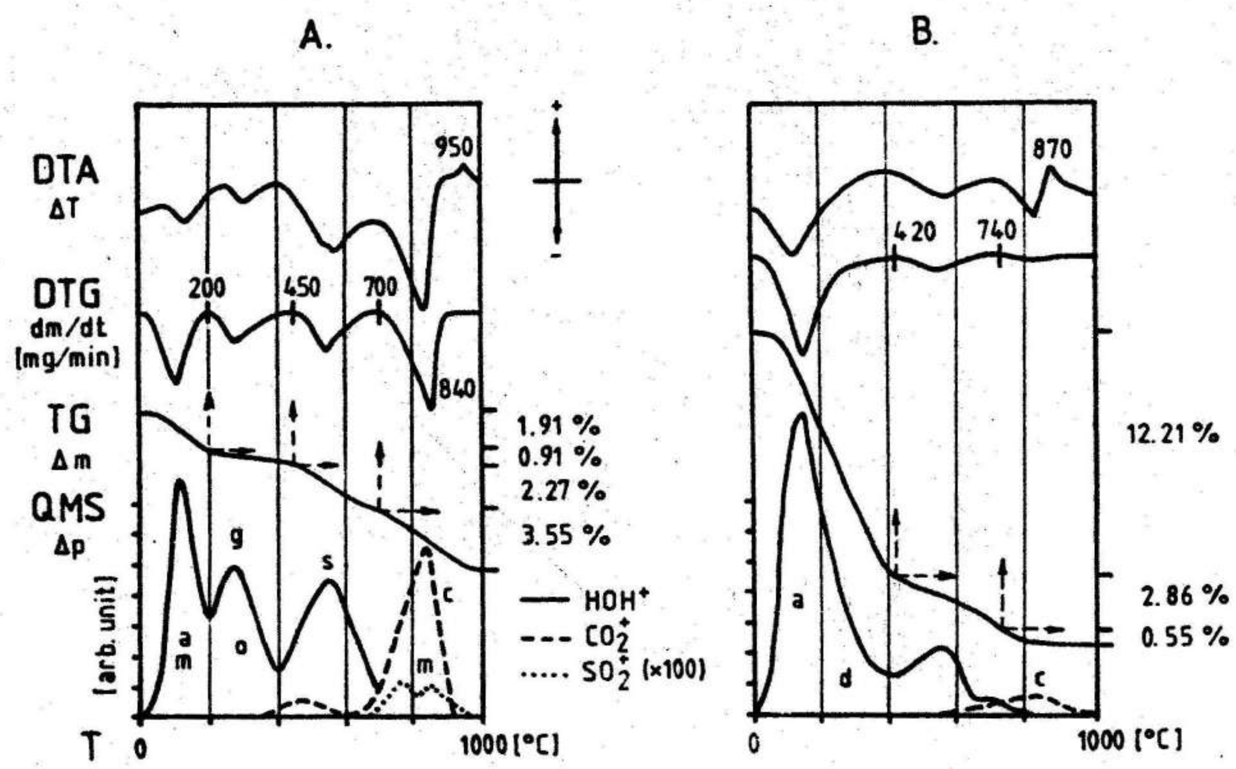

FIGURE 5. Mineral paragenesis of serpetinite, from Bogoslovac, Yugoslavia (A), Trodos, Cyprus (B), Bódvaráko, Hungary (C) and Tacajo, Cuba (D)
a = antigorite, ch = chrysotile, b = brucite, m = magnesito-calcite

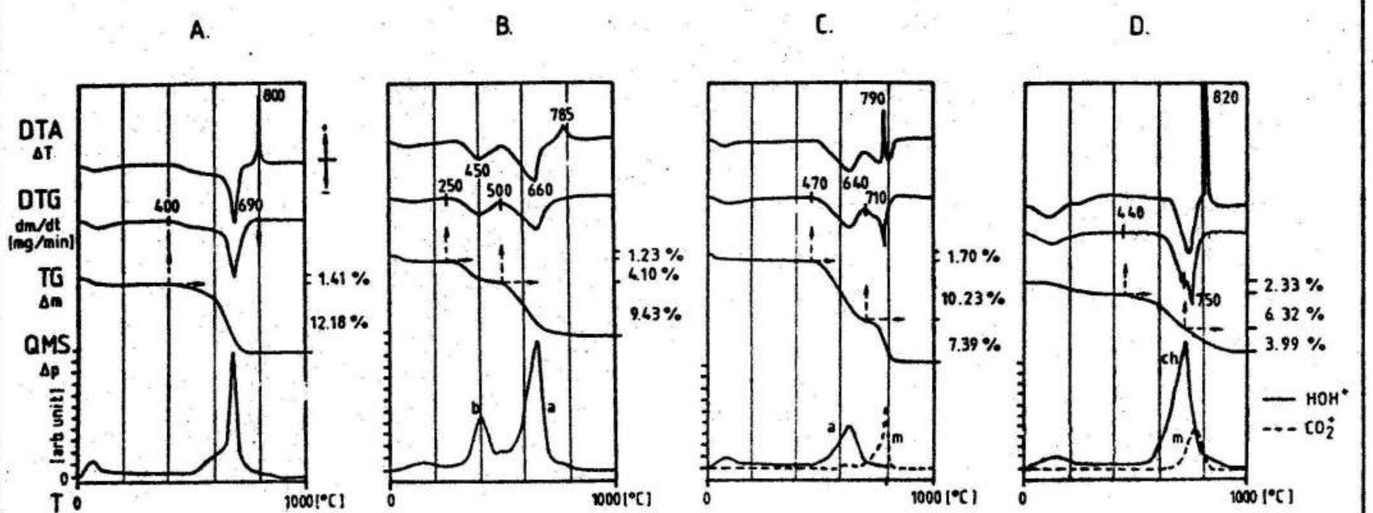

FIGURE 6. Mineral paragenesis of a brick clay from Great, Hungarian Plain (A) and an important tuffigene raw material, beidellite from Banes, Cuba (B)
a = amorphous material, c = calcite, d = dioctahedral smectite, g = goethite, m = mirabilite, s = interstratified mica-smectite, o = organic material

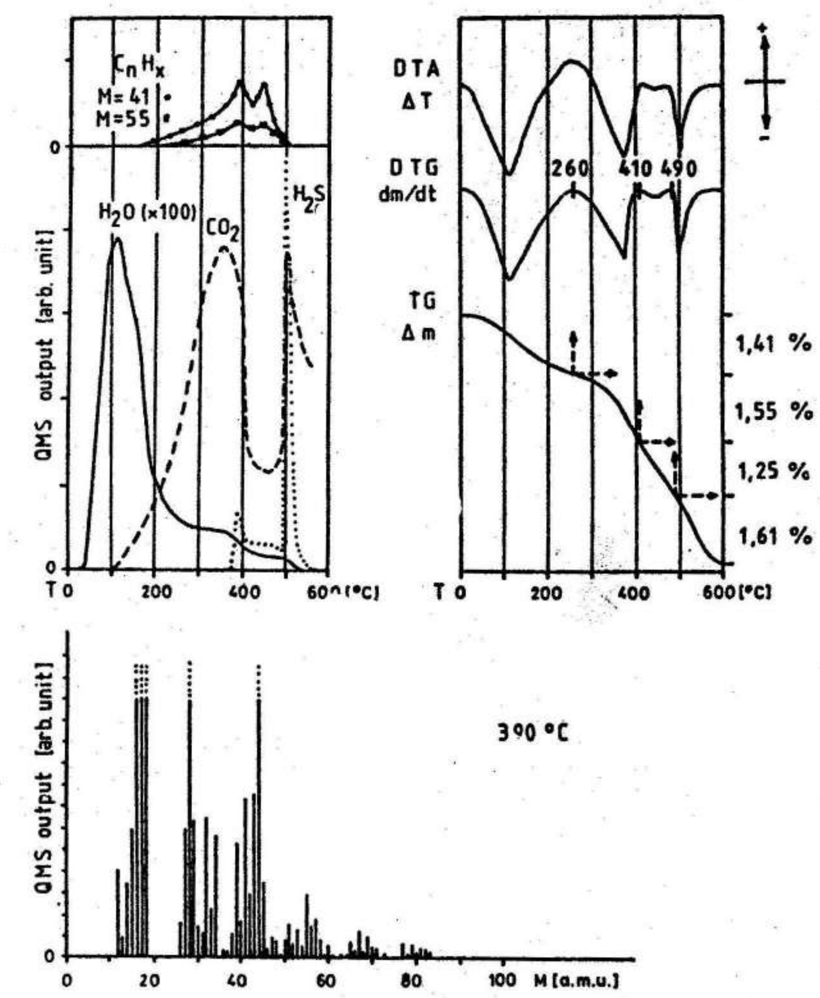

FIGURE 7. DTA, DTG, TG, QMS-EGA analysis of argillaceous aleurite ("oil shale") from Teresztenye, Hungary. H_2O, CO_2, H_2S, mass number (M) 41 and 55 were continuously detected, complete mass spectrum at 390 °C (in Heatmosphere with some air-contamination).

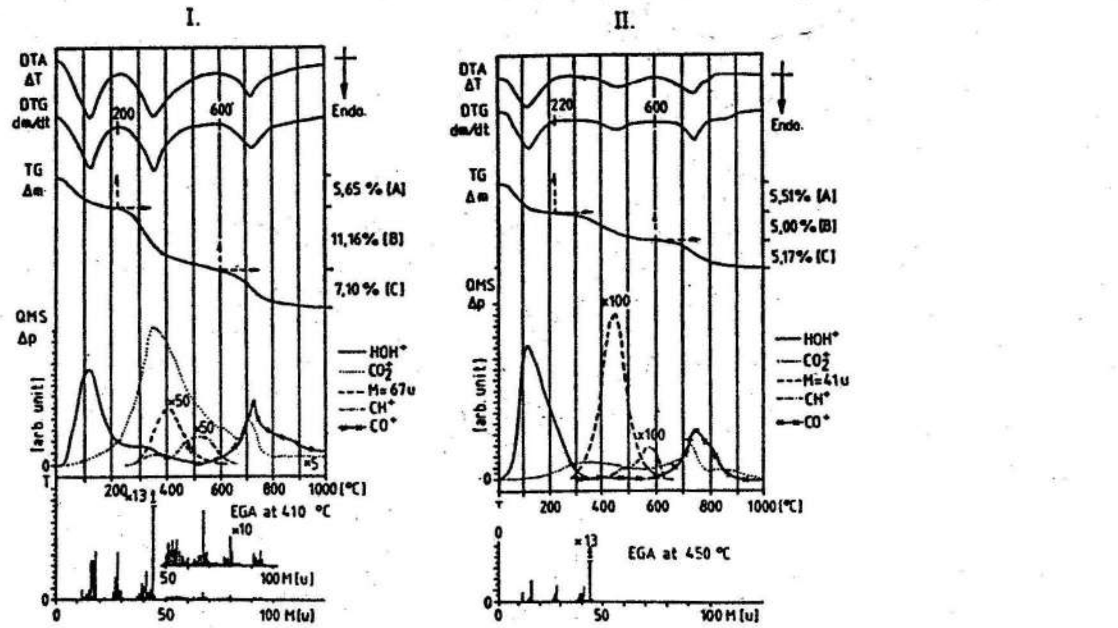

FIGURE 8. DTA, DTG, TG, QMS-EGA analysis of sporadic finds (bones).
I. = 20 000 and II. = 100 000 years old (B.P.).

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CONJETURAS ACERCA DE LA ESTRUCTURA INTERNA DEL PLANETA
CONJECTURES ABOUT THE INTERNAL STRUCTURE OF THE PLANET

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RESUMEN: En el presente trabajo se hace un análisis de las posibles causas que dieron lugar a la formación de las tres geósferas fundamentales del planeta (corteza terrestre, manto y núcleo), como es el caso de las fuerzas cósmicas al actuar sobre la velocidad de rotación del planeta y esta a su vez sobre el material fundido de la tierra.

ABSTRACT: In the present work, an analysis is being carried out on the possible causes that gave rise to the three fundamental Geospheres of the planet (earth's crust, manto and the nucleas) as is the case with the cosmic forces that act on the rotation velocity of the planet and at the same time on the fused matter of the earth.

En la geotectónica existen abundantes hipótesis que abordan la directividad general de desarrollo de la tierra de modos contrarios, como causas de este desarrollo se consideran factores muy diversos. La mayor parte de las hipótesis contemporáneas se originan en los albores de la geología científica, perfeccionándose gradualmente a medida que progresa el conocimiento y a veces entrando de nuevo en escena tras un período de olvido temporal, de ordinario después de un fracaso de la hipótesis que había gozado del mayor reconocimiento [2].

Entre las hipótesis geotectónicas se encuentran las clásicas como la hipótesis de la Contracción, de la Tierra en Expansión, de los Flujos Subcorticales de Convección, la Rotativa, etc, y entre las contemporáneas la hipótesis de la Diferenciación a Profundidad, de la Tierra en Expansión, la Tectónica de Placas, etc. Pero en la geotectónica no conocemos la existencia de una hipótesis general que aune todos los fenómenos geológicos y derivados de estos, que plantee cual es la causa geológica fundamental que provoca determinados efectos, los que a su vez son las causas de otros procesos.

En este trabajo intentamos acercarnos a una hipótesis, sobre la que continuamos trabajando, y de la cual aquí damos algunos preliminares; acerca de las posibles causas que dieron lugar al surgimiento de la estructura interna del planeta y la relación que ésta tiene con las estructuras de menor escala planetaria.

Primeramente creemos necesario realizar una pequeña introducción filosófica del problema con vistas a esclarecer la comprensión del trabajo.

La ley de la causalidad es una ley universal del mundo material, esto significa que no hay ni un solo fenómeno que no se someta a esta ley, que se origine en contra de ella o que no tenga su fuente material correspondiente. La ley de la causalidad no tiene excepciones; si ha sucedido algo, ha pasado algo, hay que buscar su causa, sin esta no surge nada en el mundo.

Entre la causa y el efecto se establece una interacción que implica una dependencia recíproca de la causa y el efecto, su influencia mutua. El papel decisivo lo desempeña la causa, esta es precisamente la que determina la relación entre la causa y el efecto dado, desempeñando este último un papel importante, pero con todo secundario.

La causa y el efecto no deben conceptuarse aislados, sino en relación con los fenómenos que los han originado o que han sido originados por ellos. Entonces un mismo proceso u objeto es simultáneamente la causa y el efecto. En relación con el fenómeno que ha provocado es la causa, pero con respecto al fenómeno que lo ha engendrado es ya efecto. La causa y el efecto son eslabones de la complicada cadena de objetos y fenómenos que actúan unos sobre otros.

F. Engels planteó: "En el mundo existen una interacción universal: consiste en que la causa y el efecto cambian continuamente de lugar; lo que aquí o ahora es la causa, se convierte allí o entonces en efecto y viceversa." [3].

En esta complicada cadena de relaciones entre las causas y los efectos tiene mucha importancia separar las causas fundamentales [3].

Mientras se desconocen las causas principales se hacen muchas conjeturas, esta es una más.