THERMOANALYTICAL CURVES FOR YAMATO-74013 AND -74010 DIOGENITES

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Abstract: Within a thermoanalytical study of a number of meteorites were obtained differential thermal (DTA) and thermogravimetric (TG) curves for the Yamato-74013 and -74010 diogenites. Small lithic fragments (blebs) and fines were taken for samples, occasionally weathered. Heating both in air and oxidation-suppressing in Ar was applied up to 1200°C, but the interval not exceeding 700°C appeared relevant for analysis. The thermoanalytical data were tabulated. The major features on the DTA-curves were found to originate from oxidation of troilite to pyrrhotite and magnetite, being followed by further partial oxidation of magnetite to maghemite and hematite. The consistence was shown of the thermoanalytical and thermomagnetic data, while possible interference of thermal effects with magnetic properties of minerals hypothesized. The similarity of the thermoanalytical curves for both diogenites examined suggests the support to the view that they came from a single fall.

1. Introduction

Thermoanalytical study of a number of meteorites of various types suggested that such a study when careful enough and appropriately correlated is capable to retrieve an independent mineralogical-petrological information possibly useful for meteorite research (LANG *et al.*, 1981).

However, despite its relative simplicity and a small amount of material as required for the measurements, the method as applied to unweathered water-free rocks in recent years proved to be rather little attractive (SMYKATZ-KLOSS, 1982). The reason is the often uneasy explanation of the DTA-curves, sometimes too laborious to be of practical use. It may be reminded that the DTA-curves for rocks are not obtained as simple superposition of those for single mineral components. The features due to the latter, especially to the minor ones, not to mention the trace minerals, can be perturbed, deformed and/or shifted, if not to become hidden—disappear. Sample heating under access of air can lead to unwanted biasing thermal effects from oxidation processes.

Under such circumstances a phenomenological approach is often preferred hardly stimulating the interest in the method.

To the knowledge of the present authors the DTA-curves for meteorites are not available, with a few exceptions. Recently GOODING used them for explanation of the mineralogical aspects of the terrestrial weathering of samples of Holbrook and three ALHA chondrites (GOODING, 1981).

Starting our thermoanalytical study of the Yamato-74013 and Y-74010 diogenites we accounted their relevance for such a study: we found their advantage in the apparently small number of the accessory opaque minerals—chromite, troilite and kamacite—making together 3.4 wt% against 96.4 wt% predominance of orthopyroxene as the major mineral. The availability of the detailed chemical and mineralogical-petrological characterization of the diogenites (see TAKEDA *et al.*, 1978, 1981; YABUKI *et al.*, 1978; LANG *et al.*, 1980; MASUDA *et al.*, 1981) seems to provide a reasonable basis for the search for explanation of the thermoanalytical data, possibly extended to the data from the thermomagnetic analysis (NAGATA and SUGIURA, 1976; SUGIURA, 1977).

2. Experimental

The specimens of the Y-74013 and Y-74010 diogenites were received from the National Institute of Polar Research (Tokyo). Small lithic fragments of the Y-74013 diogenite were analyzed as obtained from crushing a larger specimen, occasionally powdered by grinding in an agate mortar. Only powdered samples of the Y-74010 diogenite were taken for analysis.

The DTA- and TG-curves were obtained with Rigaku Denki Thermocontroller. High purity Al_2O_3 was used as reference material. Heating up to 1200°C and cooling down were performed at the rate of 10°C per minute. The simultaneous assessment of the thermal differential and thermogravimetric curves was possible only for heating under free access of air. In the atmosphere of argon the thermogravimetric measurements were excluded.

3. Results

In Fig. 1 the dilatometric curve is shown for a lithic fragment of the Y-74013 diog-

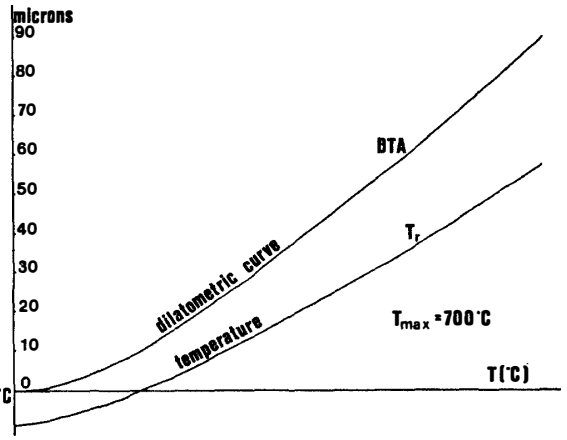


Fig. 1. Dilatometric curve for a lithic fragment of the Y-74013 diogenite of length of 6.76 mm. Vertical axis: length increments in microns. Horizontal axis: temperature unscaled. The rise of temperature traced by the lower curve.

enite. Its smooth appearance and nearly linear rise prove the insensitivity of the expansion of the silicate matrix to the contributions of the included minor mineral components—a quasi monomineralic behavior of the bulk sample.

In Figs. 2–4 are given the thermoanalytical curves for the powdered samples of the Y-74013 diogenite. The features on the curve in Fig. 2 are seen significantly changed in Fig. 3, the latter curve being obtained for a powdered sample stored at room tem-

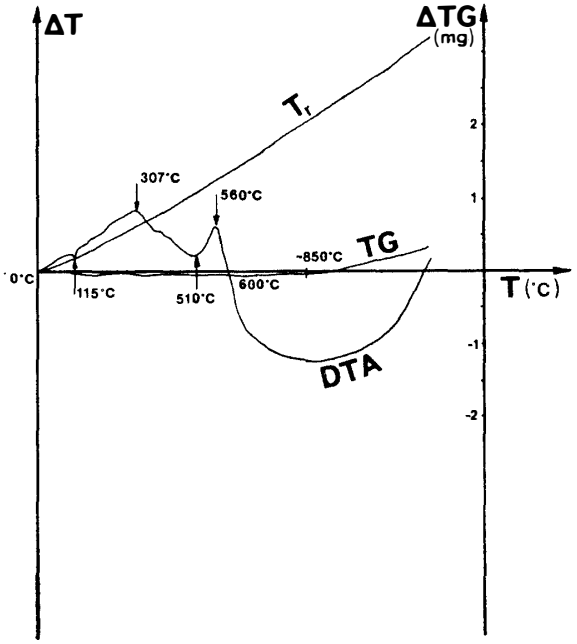
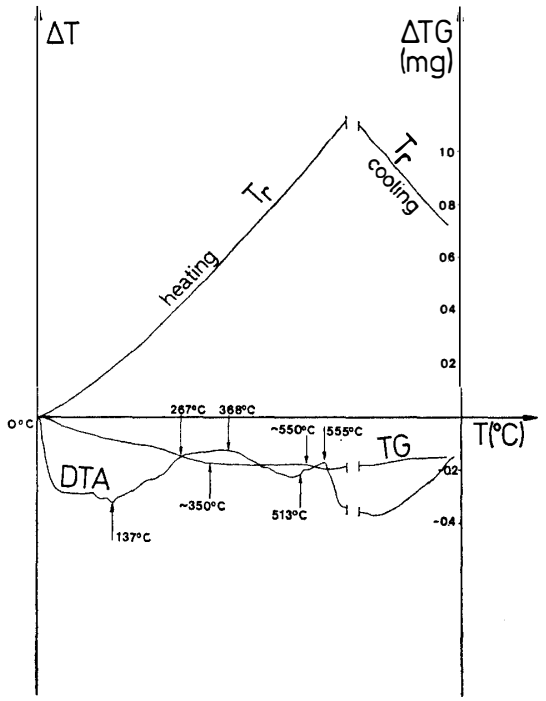


Fig. 2.



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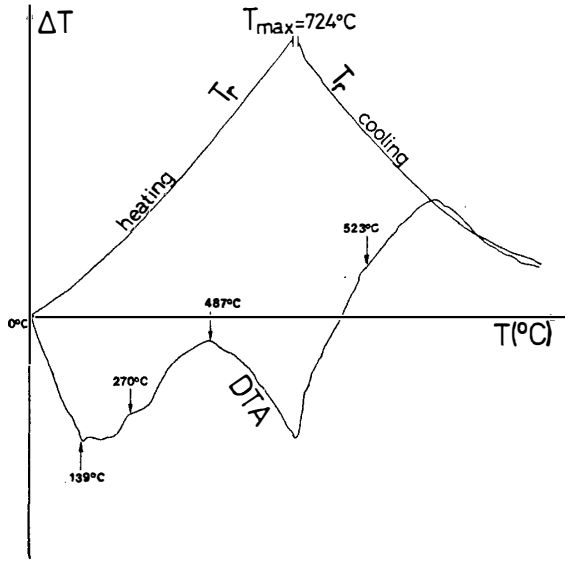
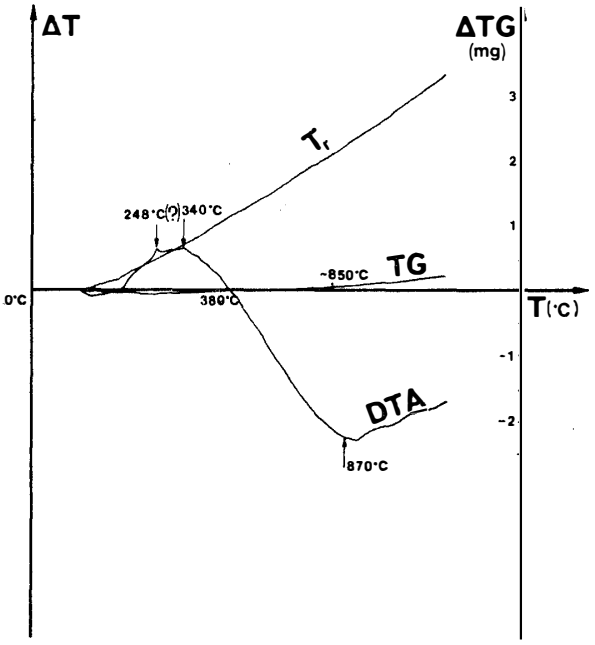


Fig. 4.



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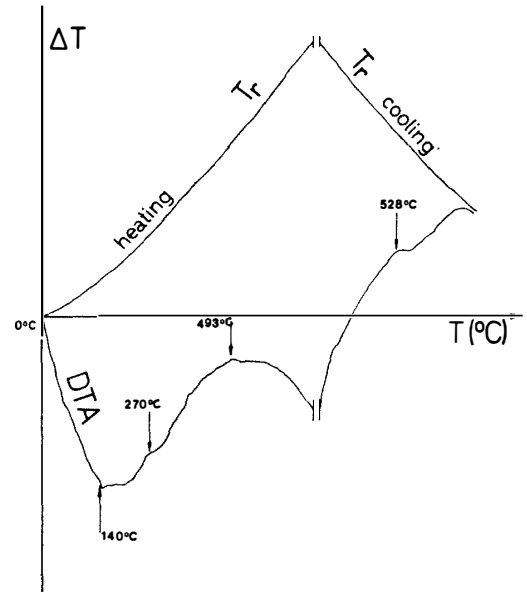

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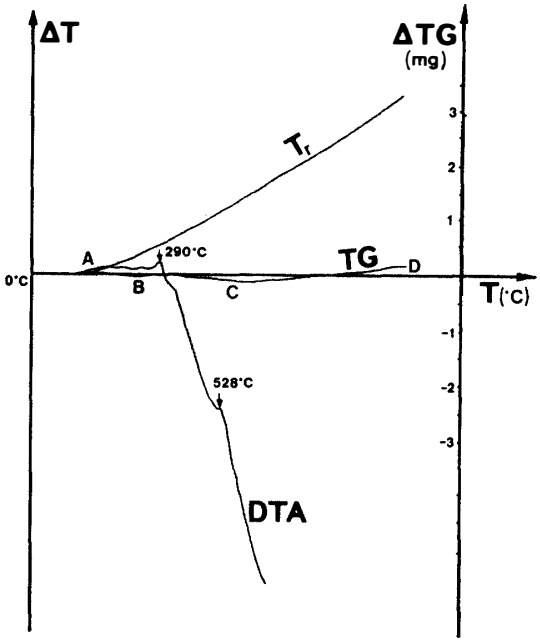

Fig. 7.

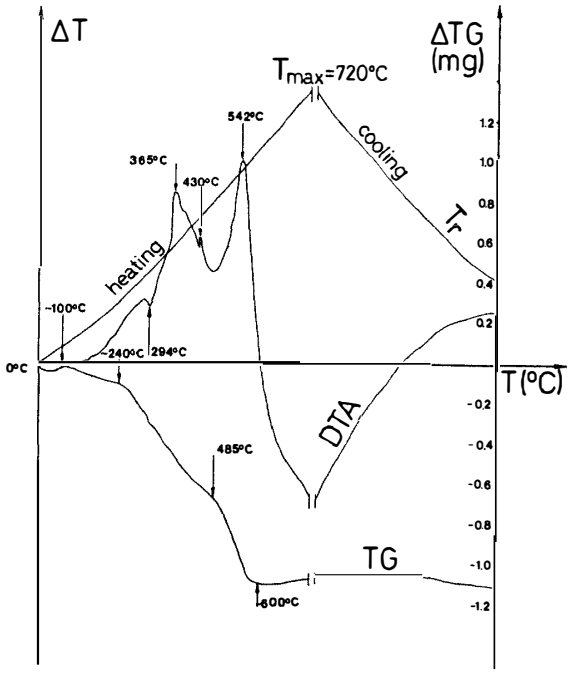

Fig. 8.

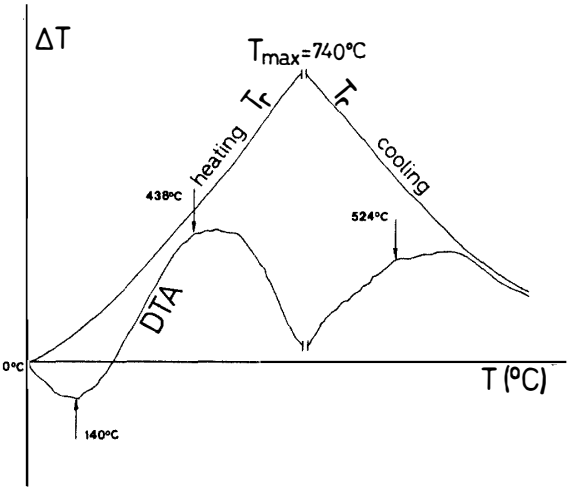

Fig. 9.

Figs. 2–9. Thermoanalytical curves for the Y-74013 (Figs. 2–6) and Y-74010 (Figs. 7–9) diogenites. Left Y-axis: ΔT in arbitrary units. Right Y-axis: ΔTG scaled in milligrams. The rise and fall of temperatures traced with T_r curves. For explanation see Table 1. Explanation of the cooling branches omitted in table is given in the text.

Table 1. Thermoanalytical data for the Y-74013 and Y-74010 diogenites.

	Y-74013					Y-74010		
Sample	pwd air	pwd wtd air	pwd wid Ar	lf air	lf Ar	pwd air	pwd wtd air	pwd wtd Ar
Figure in text	2	3	4	5	6	7	8	9
Mass (mg)	34.64	48.90	50.31	31.16	49.70	17.60	32.00	33.56
t°C	ΔT ΔTG	ΔT ΔTG	ΔT	ΔT ΔTG	ΔT	ΔT ΔTG	ΔT ΔTG	ΔT
20	20	20		20		20	20	
100	115 PEnW	139 PEn	139 PEnW		140 PEnW	−0.28%		140 PEn WW
200		−0.4%		248 PExW		230	−3.28%	
300	307 BEn	267 B	270 PExW W+BEx	340 BEn	270 PEx WW	290 P+B (Ex+En)	294 PEn	
400	−0.3%	368 BEn 360				−0.4%	365 PExL+BEn 430 PExW	438 PExW W+B En
500	510 BEx	513 PExWW	487 BEn	+0.64%	493 BEn	528 PExWW		
600	560 PExL	555 PEx+BEn WW				570	542 PExLL+BEn 600	
700							const	
800	850					+1.13%		
900				870 BEx				
1000	+1%			1200				

Sample; lf: lithic fragment, pwd: powdered (fines from sample grinded in an agate mortar), wth: weathered (fines stored in a test tube at room temperature without any special precaution for 2 years), air, Ar: heated in the atmosphere of air, Ar. t°C: In this column the level of temperature is indicated. ΔT: In this column the temperatures of the respective features are specified. P: Peak on the DTA-curve. Ex, En: Exothermic, endothermic. L, LL: Large, very large. W, WW: Weak, very weak. B: Bending point. BEx, BEn: Bending towards exothermicity, endothermicity. ΔTG: Mass losses specified in wt %, arrows indicate the involved temperature intervals, the ends of the intervals are given with numbers.

perature without any special precaution in a test tube for about 2 years. The weathering-produced enrichment of this sample in volatiles has been recorded as mass loss on the TG-curve. With suppressed oxidation by heating in the atmosphere of Ar the curve for the same weathered material is very different (Fig. 4). It resembles the curves for the lithic fragments which are shown in Figs. 5 and 6. The curve in Fig. 6 refers to heating in Ar.

The curves as shown in Figs. 7–9 were obtained for powdered samples of the Y-74010 diogenite. Figure 8 refers to a powdered sample stored in the same way as the sample whose curves are shown in Fig. 3. Comparing the DTA-curve from Fig. 8 with that from Fig. 3 we find the former much richer in features than the latter. This enrichment in features and remarkable mass loss recorded on the TG-curve argue for amplified volatilization of products of more advanced weathering.

To facilitate the analysis of the obtained thermonalytical data we tabulated them in Table 1—for the Y-74013 and Y-74010 diogenites respectively. The tabulated data refer to heating only, while those for cooling being accounted in the discussion are not specified in the tables.

4. Discussion

Our discussion starts from a few remarks supporting the further attempt to explain the obtained results.

With a thermoanalytical curve is monitored the response of the analyzed material to heating (or cooling). In diogenites heating affects both the pyroxene matrix and the grains of minor mineral components distributed inside. Looking at the curves one can see that instead of the full range it is enough to consider the temperature interval from 20°C to 700–800°C. At these temperatures the pyroxenes remain chemically unchanged. Apart from the literature data (*e.g.* ATLAS, 1952; SCHWAB, 1969; GROVER, 1972; SMITH, 1974) we proved it by heating a lithic fragment of the Y-74013 diogenite up to 700°C sealed in vacuum in a quartz ampoule. The diffractogram for this fragment when compared with those for the unprocessed samples of both Y-74013 and Y-74010 diogenites has shown rather insignificant alteration of lines for pyroxene and chromite. Thus from heating of pyroxene no detectable thermal effect can be expected, neglecting the very small one for the transition of enstatite from monoclinic to orthorombic at 630°C.

Chromite is more difficult to handle. With the data from electron microprobe for elemental abundances in chromite as reported by TAKEDA *et al.* (1978) we realize that some part of the Fe^{2+} ions in this spinel is replaced by the equivalent Mg^{2+} and Mn^{2+} ions, while that of Cr^{3+} by Al^{3+}, Ti^{3+} and Fe^{3+} ions, filling the octahedral B sites of the respective sublattices. Because the temperature of the Curie point is strongly dependent upon the composition of the spinel (see ROBBINS *et al.*, 1971; WASILEWSKI *et al.*, 1975), with our data we can suppose the Curie point of chromite in the examined diogenites to be well below the room temperature.

Another problem arises with regard to kamacite. Its abundance is as high as 0.1% (TAKEDA *et al.*, 1978) but specified as iron Co-rich and Ni-poor, with Curie point at 792°C (see NAGATA and SUGIURA, 1976). Thermoanalytical response to this transi-

tion can be expected.

At 140°C the α-phase transition of antiferromagnetic hexagonal troilite occurs (BRODSKAYA *et al.*, 1973). This transition is recorded as a very small endothermic peak on the curves in Figs. 2, 3, 4, 6 and 9, and detected as feature on the thermomagnetic curves aI at 152°C and cI at 150°C (LANG *et al.*, 1980). Because the curves in Figs. 4, 6 and 9 were obtained from heating in Ar, it can be concluded that by suppressing oxidation we made the detection easier, minimizing or even nullifying the shift of the recorded temperatures which are 139, 140 and 140°C respectively.

The oxidation of troilite to pyrrhotite and magnetite was discussed in the literature only with reference to carbonaceous chondrites. The pertinent references and the summary of the discussion considering its cosmochemical aspects are to be found in the contribution of HERNDON *et al.* (1975). However, before going to the observed thermoanalytical consequences which are believed to follow the oxidation of troilite, we have to characterize the DTA-curves more generally.

With rising temperature they meander, and this makes the assessment of features, mostly in the case of small effects, difficult and uncertain. The meandering is due to distinct variation with temperature of heat capacities and diffusivities of examined and reference materials. It should be reminded that in diogenites the accessory minerals below their Curie or Néel points are all magnetically ordered: kamacite and iron are ferromagnetic, sulfides antiferro- and ferrimagnetic, chromite ferrimagnetic. Thermal properties of minerals can be strongly affected by magnetic order.

The oxidation of troilite to pyrrhotite is assumed by us as the first step in the sequence of chemical transformations in diogenite samples resulting from heating. Under free access of air pyrrhotite can be further oxidized to yield evolving SO_2. The volatilization of the latter is observed presumably on the TG-curves for the weathered samples as remarkable mass losses. Such a mass loss is less drastic to the sample of the Y-74013 diogenite, where it is as high as -0.4 wt% reached at 350°C (Fig. 3). It appears more drastic to the sample of the Y-74010 diogenite as shown in Fig. 8, reaching the total of -3.3 wt% at 600°C through the intermediate steps at 240 and 485°C.

During heating the magnetization of the non-oxidized antiferro- or ferrimagnetic pyrrhotite rises (about 180°C)—as the result of redistribution of iron vacancies—then decreases to reach its Curie point at 320°C. In the same time at 150°C begins the oxidation of magnetite. The structure of the inverse spinel makes the properties of magnetite very sensitive to substitution of both Fe^{2+} and Fe^{3+} ions by other di- and trivalent ions. They are also sensitive to the size of grains in which magnetite occurs. This problem was examined by EGGER and FEITKNECHT (1962), who using DTA-curves found that in the atmosphere of oxygen oxidation of magnetite results in its conversion to γ-Fe_2O_3 maghemite at lower temperatures, or to α-Fe_2O_3 hematite at higher ones. The transition of metastable maghemite to more stable hematite occurs between 500 and 600°C. While the Curie point for pure magnetite is 580°C, that for α-Fe_2O_3 is 600°C.

Confronting the DTA-curves we suggest to refer the features at 267 (Fig. 3), 270 (Fig. 4), 248 (Fig. 5), 270 (Fig. 6), 290°C (Fig. 7) to the transition of magnetite to metastable maghemite. The scattering of temperatures can be explained with such factors as varying composition, shape and size of respective mineral grains, not excluding the varying *in situ* oxidation potential.

The bending points at 307 (Fig. 2), 367 (Fig. 3) and 340°C (Fig. 5) reflect possibly the bulk change in thermal properties of the material governed at these temperatures presumably by the thermoanalytical joint behavior of pyrrhotite and magnetite. The broad bendings at 487 (Fig. 4), 493 (Fig. 6) and 438°C (Fig. 9) were obtained for suppressed oxidation. The nature of these bendings seems to not differ from that materialized in bendings observed between 300 and 400°C on the curves for samples heated in air. The broad bending at lower temperatures seems to originate from an increased transient contribution in samples of the oxidized chemical species.

The very small endothermic peaks at 510 (Fig. 2) and 513°C (Fig. 3) are related to the Curie point of magnetite supposed to be partially substituted. Because this feature, diagnostic for magnetite, was identified also on the DTA-curves for a number of meteorites other than diogenites, we analyzed for reference a sample of natural magnetite of unknown origin and composition, applying heating in Ar. The obtained DTA-curve proved the occurrence of an endothermic peak at 557°C on the heating branch and an exothermic peak at 551°C—unquestionable evidence for a reversible polymorphic transition. With the reference calibrating line as reproduced by SMYKATZ-KLOSS (1982) we estimated this magnetite to be substituted by 7 wt%. Applying an extensive extrapolation to the above line we approximated the substitution level in magnetite from diogenites as of some 20–25 wt%. It should be emphasized that in Figs. 4, 6 and 9, *i.e.* for heating in Ar, the endothermic peaks appeared too small to be detected on the heating branches and only extremely weak ones at 523, 528 and 524°C exothermic were assessed on the cooling branches. However, in Fig. 7 the small peak on the heating branch is exothermic (at 528°C) and the same refers to some cases not shown

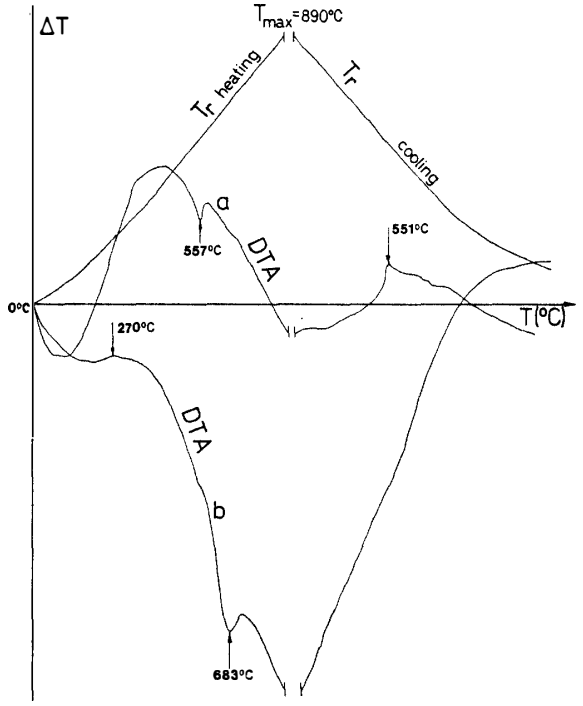

Fig. 10. DTA-curves for heated in Ar samples of natural (a) magnetite and (b) chromite. Axes labelled as previously.

here (metal phase of the Marjalahti pallasite, bulk and metal phase of the Łowicz mesosiderite, bulk sample of the Krymka LL3 chondrite, matrix of the Bjurböle L4 chondrite). The ambiguity of the considered feature needs a further thorough study.

We also obtained the DTA-curve for a sample of natural chromite of unknown origin and composition heated in Ar (b in Fig. 10). The endothermic peak at 683°C on the heating branch disappeared on the cooling one. This is due presumably to the irreversible change of the spinel structure.

The last effect of interest encompasses the exothermic peaks as occurring at 560 (Fig. 2), 550 (Fig. 3) and 542°C (Fig. 8). Similar peaks were observed for a number of meteorites, often conspicuous—the largest on the DTA-curves. In all cases they were obtained in oxidizing atmosphere. We suspect the already discussed transition from metastable maghemite to hematite to be responsible for this feature. The answer to this question would be reached with better understanding of the thermoanalytical curves for meteorites other than diogenites.

5. Conclusions

Thermal effects at heating and cooling both exo- and endothermic were assessed

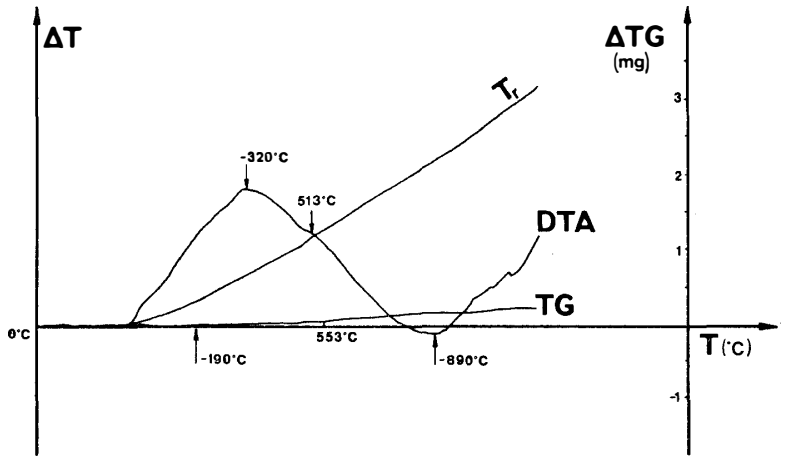

Fig. 11.

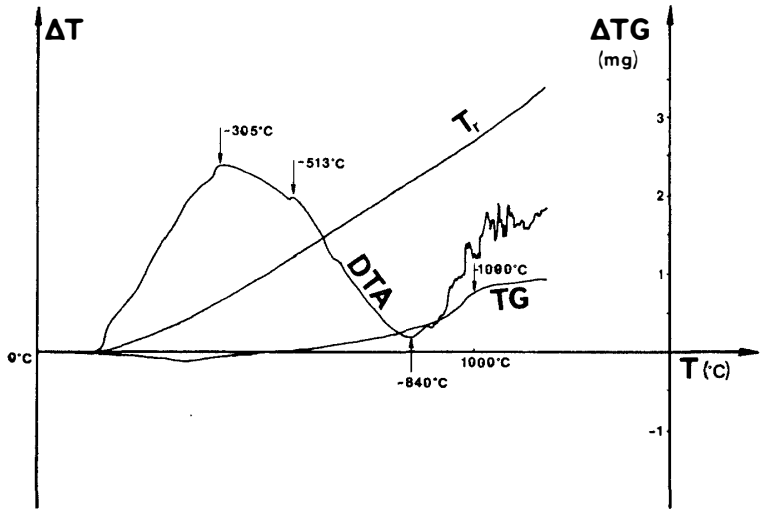

Fig. 12.

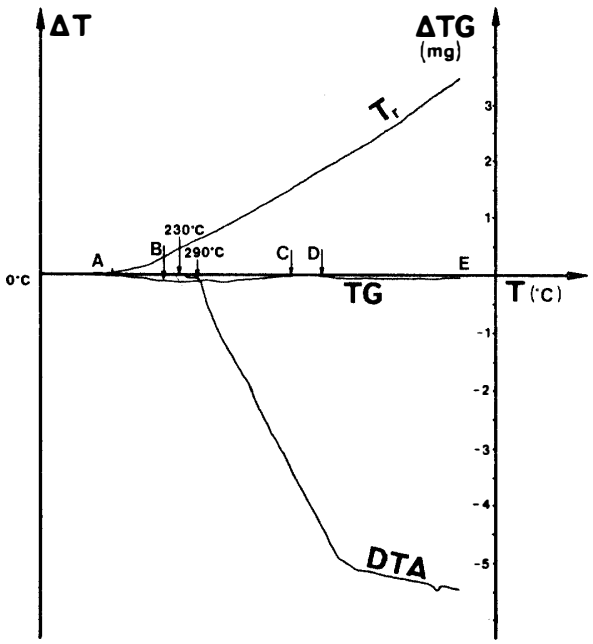

Fig. 13.

Figs. 11–13. Thermoanalytical curves for Adhi Kot E4 enstatite chondrite (Fig. 11), Staroe Pesyanoe (Fig. 12) and Norton County (Fig. 13) both aubrites. Axes labelled as previously.

in samples of the Y-74013 and Y-74010 diogenites. They appear as both common and individual features on the DTA-curves, aided in some cases with the TG-curves. As common can be recognized the shapes of the curves as obtained under oxidation-suppressing conditions.

Our main conclusion is the key role of chemical transformation of troilite in the thermal effects as observed between 150 and 550°C. For the importance of troilite as mineral component of meteorites such a conclusion is rather challenging. But we are far from putting it beyond any debate.

We obtained near identical curves for blebs (Fig. 6) and fines (Fig. 4) from the Y-74013 diogenite and also from the Y-74010 (Fig. 9). This finding can probably be used as an independent argument in favor of the view that both diogenites examined by us came from a single fall (see TAKEDA *et al.*, 1981).

However, we must be careful with all diagnostic conclusions because the thermo-analytical curves for *e.g.* Adhi Kot E4 enstatite chondrite (Fig. 11) and Staroe Pesyanoe aubrite (Fig. 12) do not differ much between themselves and resemble that in Fig. 5. In turn the curve for the Norton County aubrite (Fig. 13) does not much differ from that shown in Fig. 7.

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