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Low level detection and quantification of carbonate species using thermogravimetric and differential thermal analysis

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Low level detection and quantification of carbonate species using thermogravimetric and differential thermal analysis

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Front cover

TGA/SDTA sample robot.

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Foreword

This report is the published product of a study by the British Geological Survey (BGS) and was produced under the Science Facilities' Maintenance and Development of Capability (MaDCap) project.

This report aims to provide a procedural manual for the newly acquired simultaneous thermogravimetric and differential thermal analysis system and details of initial testing to determine the low level detection and quantification of carbonate species.

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Summary

This report describes a procedural manual for the newly acquired simultaneous thermogravimetric and differential thermal analysis system and details of initial testing to determine the low level detection and quantification of carbonate species. This work was carried out as part of the Science Facilities' Maintenance and Development of Capability (MaDCap) project.

The report firstly introduces the techniques of thermal analysis and BGS's capabilities in this area. The report then details a series of experiments designed to determine the low level detection and quantification of carbonate species (calcite, dolomite and siderite).

Results indicate that combined TGA-DTA analysis offers significantly lower levels of detection than other mineralogical techniques such as X-ray diffraction analysis.

Measured carbonate species concentration levels as low as 200 ppm (dolomite and siderite) and 150 ppm (calcite) in synthetic mixtures are proved. Lower detection limits are possible but proving these is precluded by the difficulty of handling/weighing such small quantities.

1 Introduction

The International Confederation for Thermal Analysis and Calorimetry (ICTAC) defines 'thermal analysis' (TA) as a group of techniques in which a physical or chemical property of a sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed (Hill, 1991). The more frequently used thermal analysis techniques and their uses are summarised in Table 1 (modified from Haines, 2002).

Table 1. Thermal methods

Technique	Abbreviation	Property	Uses
Thermogravimetry or (Thermogravimetric analysis)	TG TGA	Mass	Decompositions, oxidations
Differential thermal analysis	DTA	Temperature difference	Phase changes, reactions
Differential scanning calorimetry	DSC	Power difference of heat flow	Heat capacity, phase changes, reactions
Thermomechanical analysis	TMA	Deformations	Mechanical changes
Evolved gas analysis	EGA	Gases evolved or reacted	Decompositions
Thermoluminescence	TL	Light emitted	Oxidation
Thermomagnetometry	TM	Magnetic	Magnetic changes, Curie points

As with many areas of analytical science, it is unlikely that any single TA technique can provide all the information required to understand the behaviour of a sample. Instruments that provide two or more types of TA measurement at the same time (Simultaneous Thermal Analysis, STA) are therefore commonly employed (e.g. TG-DTA, TG-DSC, TG-DTA-EGA).

TA techniques are widely employed across a range of disciplines including chemistry, materials science, foods and pharmaceuticals but are more rarely employed in geological/environmental laboratories. However, as demonstrated by the BGS laboratories (see next section), thermal methods frequently provide very useful complimentary data on the mineralogy and behaviour of geological materials.

1.1 THERMAL ANALYSIS IN THE BGS

The BGS Mineralogy & Petrology laboratories have a history of carrying out geoscience-related TA research since the 1960s. In fact, the facility is certainly the premier UK institution for TA in the geosciences with a prominent international reputation established by the frequent journal publications produced during the 1970s, 80s and 90s (e.g. Morgan, 1977; Milodowski & Morgan, 1980, 1984; Warne *et al.*, 1985; Morgan *et al.*, 1986; 1988ab; Milodowski *et al.*, 1989; Inglethorpe & Morgan, 1993; Parsons *et al.*, 1997). The equipment also proved invaluable for industrial mineral development projects (e.g. Harrison *et al.*, 1998) and the characterisation of materials from UK NIREX's low level, Sellafield and Dounreay investigations (e.g. Bloodworth *et al.*, 1987; Kemp *et al.*, 1991).

However during the late 1990s and early 2000s, BGS TA activity declined due to a combination of a downturn in demand from both radwaste characterisation and industrial mineral projects, a loss of specialist staff and the restrictive nature of the 1970/80s-purchased equipment.

In order to help re-stimulate TA activity in BGS, a successful proposal was made in April 2005 to purchase a state-of-the-art thermal analysis system which would offer simultaneous thermogravimetric and differential thermal analysis (TG-DTA) and efficiency gains through a sample changer facility.

1.2 METTLER-TOLEDO SDTA851^{e} SYSTEM

The purchased Mettler-Toledo SDTA851^{e} system (Figure 1) provides the following:

- High resolution (1 µg), internally calibrated thermobalance
- Large temperature range (ambient to 1600˚C) furnace
- High temperature accuracy (±0.5˚C), calibrated by pure metal melting points
- Sample robot with 34 position sample changer allowing automatic processing and different crucible/program options (Figure 2).
- Parallel guided balance ensures accurate, position-independent weight measurements (Figure 3).
- Sample sizes up to 1000 mg in up to 900 µl crucibles
- Data collection and interpretation using STARe software suite running on dedicated PC.
- Programmable gas controller enabling two channel gas flow measurement, switching and monitoring.
- Standalone re-circulating water cooling to provide constant measuring conditions and faster cooling between samples.
- Ability to add coupled devices (e.g. FTIR spectrometer, mass spectrometer)

Figure 1. Mettler-Toledo SDTA851^{e} system installation at BGS Keyworth.

Figure 2. Detail of sample robot loading a platinum crucible

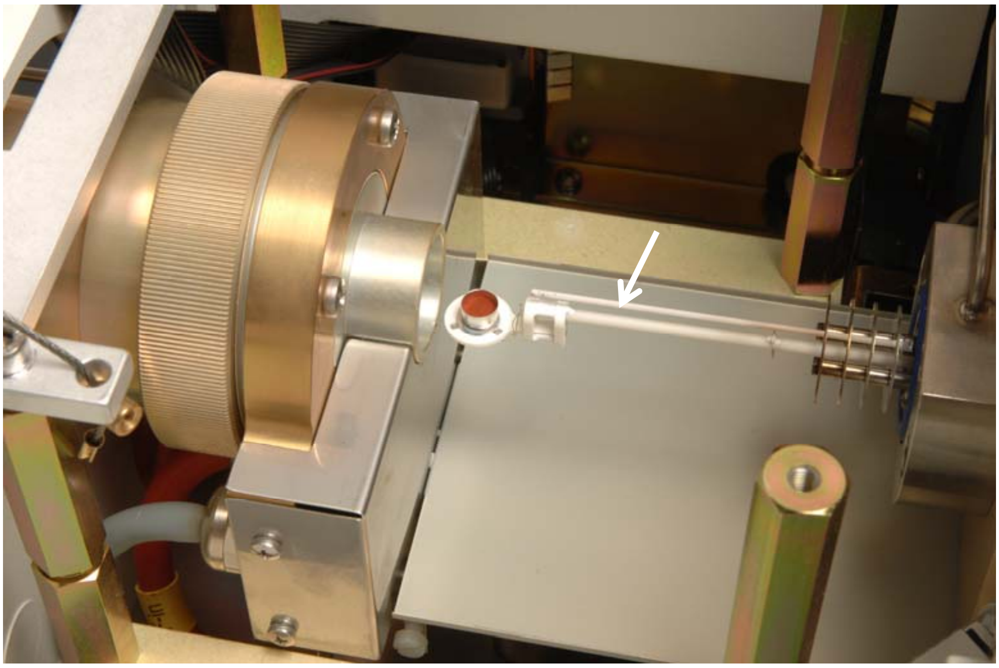


Figure 3. Crucible sitting in its measurement position on the balance arm. Note that the sample changer has been removed and furnace retracted for clarity. The reactive gas supply capillary is arrowed.

Following installation, the system has provided useful data to a variety of projects (e.g. CO_2 storage, limestone and industrial mineral assessment, contract analyses for external clients such as BPB Plc) but its potential has not been fully exploited due to a lack of R&D funding.

1.3 THERMAL ANALYSIS OF CARBONATES

The presence of carbonate species (particularly calcite, dolomite, ankerite and siderite) in geological materials can routinely be determined and quantified by powder X-ray diffraction (XRD) analyses. However, the lower detection limits afforded by XRD for such species is of the order of 0.1wt%. Thermal analysis techniques, such as coupled TG-DTA have the ability to quantify lower levels of carbonate species and so complement XRD analysis, particularly where lower levels of detection are required.

An important development in the detection and quantification of carbonate species was the use of 'variable atmosphere thermal analysis' (Warne, 1986). It was discovered that running carbonate species TA experiments in flowing CO_2, rather than N_2 or air, provided improved individual peak and reaction definition. By adopting the same purge gas as that released during sample decomposition, the carbonate species has to overcome the increased CO_2 partial pressure before decarboxylation. This results in increased decomposition temperatures and faster, more vigorous reactions over a smaller temperature range. A summary of common carbonate mineral decomposition characteristics is shown in Table 2.

Table 2. Carbonate mineral decomposition in flowing CO_2 atmosphere

Carbonate species	**Reaction**		**Temperature range (˚C)**	**Weight loss (%)**
	Step	**Equation**		
Calcite	Total	$CaCO_3 \rightarrow CaO + CO_2$	900 - 1000	43.97
Dolomite	1.	$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2$	550 - 765	23.86
	2.	$CaCO_3 \rightarrow CaO + CO_2$	900 - 1000	43.97
	Total	$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2$	550 – 1000	47.77
Siderite	Total*	$FeCO_3 \rightarrow FeO + CO_2$	450 - 550	37.99

*the siderite decomposition mechanism is strongly linked to oxygen fugacity. The data shown relates to low oxygen fugacity as would be expected to be produced by a flowing CO_2 atmosphere.

The rapid, low level detection and quantification of carbonate species afforded by TA techniques is capable of providing useful data to a wide range of BGS projects but is particularly important in studies related to CO_2 storage, from analogue and demonstration sites to supporting laboratory studies. Reactions between CO_2-rich porewaters and carbonate cements in reservoirs and/or cap rocks are relatively fast. Therefore the detection of low-levels of carbonate minerals is fundamental to understanding long-term storage processes.

This report therefore presents the results of a small study carried out during 2008/09 under the Maintenance and Development of Capability (MaDCap) project which aimed to:

- familiarise BGS staff with the newly-purchased thermal analysis system
- produce a user manual
- determine the lower limits of detection for carbonate species by TG-DTA
- advertise the abilities of the new system to BGS project leaders

2 Materials and methods

2.1 MATERIALS

The following ‘pure’ mineral standards were sourced from the BGS reference collection:

- RC769/1 Siderite (Ivigtut, Greenland)
- RC193/1 Dolomite (Larangwe, Blantyre District, Malawi)
- RC194/1 Calcite (Canada)
- RC191/1 Calcite (Eire)

together with:

- GSR-12 Dolomite (mineral standard from BGS XRFS laboratories)
- Quartz (BGS XRD lab, locality unknown)

2.2 SAMPLE PREPARATION

A representative sub-sample of each sample was removed and then hand-crushed in a pestle and mortar. The crushed material was then ball-milled to <0.125 mm.

2.3 CHARACTERISATION OF MINERAL STANDARDS

To identify whether the selected materials were suitable for this study, each was firstly mineralogically examined using XRD analysis followed by major element geochemical analysis by X-ray fluorescence spectroscopy (XRFS).

2.3.1 X-ray diffraction analysis

In order to provide a finer and uniform particle-size for whole-rock XRD analysis, a *c*.3 g portion of the ball-milled material was wet-micronised under acetone for 10 minutes, dried, disaggregated and back-loaded into standard stainless steel sample holders for analysis.

XRD analysis was carried out using a PANalytical X’Pert Pro series diffractometer equipped with a cobalt-target tube, X’Celerator detector and operated at 45kV and 40mA.

The samples were scanned from 4.5-85°2θ at 2.76°2θ/minute. Diffraction data were initially analysed using PANalytical X’Pert HighScore Plus Version 2.2a software coupled to the latest version of the International Centre for Diffraction Data (ICDD) database.

Following identification of the mineral species present in the samples, mineral quantification was achieved using the Rietveld refinement technique (e.g. Snyder & Bish, 1989) using PANalytical HighScore Plus software. This method avoids the need to produce synthetic mixtures and involves the least squares fitting of measured to calculated XRD profiles using a crystal structure databank. Errors for the quoted mineral concentrations are typically ±2.5% for concentrations >60 wt%, ±5% for concentrations between 60 and 30 wt%, ±10% for concentrations between 30 and 10 wt%, ±20% for concentrations between 10 and 3 wt% and ±40% for concentrations <3 wt% (Hillier *et al.*, 2001). Where a phase was detected but its concentration was indicated to be below 0.5%, it is assigned a value of <0.5%, since the error associated with quantification at such low levels becomes too large.

2.3.2 X-ray fluorescence spectroscopy

For geochemical analysis, the ground samples were dried at 105°C before fusion and determination of loss on ignition (LOI). To determine the LOI, samples were heated in a muffle furnace for 1 hour at 1050˚C. Approximately 1 g of sample was weighed accurately into a porcelain crucible. The crucible was weighed before and after heating and the two weights compared. The resulting relative loss in sample weight was reported as the LOI.

Fused beads were prepared by fusing 0.9000 g sample plus 9.000 g flux (66/34 $Li_2B_4O_7$ and $LiBO_2$) at 1200°C. All samples were analysed using these conditions for internal consistency within the batch. After fusion the melt was cast into a 40 mm fused glass bead, which was then analysed by XRFS.

The XRFS spectrometer used was a Philips MagiX Pro fitted with a 60 kV generator and 4 kW rhodium (Super Sharp) end–window X-ray tube controlled via PC running PANalytical SuperQ XRF application package. The PANalytical calibration algorithm is used to fit calibration curves and inter-element effects are corrected by theoretical alpha coefficients, calculated by the PANalytical method. All spectral backgrounds and peaks are corrected for instrument drift using two external ratio monitors.

2.3.3 Results

The results of initial characterisation of the project materials by XRD and XRFS are summarised in Tables 3 and 4.

XRD analysis of sample 'RC193/1 Dolomite (Larangwe, Blantyre District, Malawi)' showed that although dolomite formed the major component of this material, significant quantities of quartz, calcite and undifferentiated mica species were also identified. No further analyses were therefore carried out on this sample and it was removed from the investigation.

XRD and XRFS analyses indicated that the remaining samples were of sufficient purity for their inclusion in the study.

2.4 THERMAL ANALYSIS

Prior to commencing analyses, the TG-DTA system was calibrated using the specified Indium/Aluminium (In/Al) melting test. As the measured values were outside the specified limits, a total adjustment was performed and the In/Al check repeated to check compliance.

Zero runs were then completed for empty 150 µl platinum crucibles from 30 to 1100˚C in a gas flow of 80 ml/minute CO_2 at a heating rate of 10˚C/minute. However, when employing N_2 as the purge gas and CO_2 gas as the reactive gas, the TG curve showed an unaccountable weight loss at approximately 100ºC. Having excluded all the possible causes for this (new platinum crucibles, exchange of CO_2 gas cylinder and replacement gas lines in the laboratory), advice was sought from the manufacturer. Mettler-Toledo suggested that baseline runs should be performed without any crucibles under following conditions:

- N_2 protective gas and no reactive gas
- N_2 protective gas and N_2 reactive gas
- N_2 protective gas and CO_2 reactive gas
- CO_2 protective and reactive gas

The results of these runs showed that the mysterious weight loss at *c.*100 ºC was only produced with a combination of N_2 as the protective gas and CO_2 as reactive gas. Mettler-Toledo could not provide an adequate explanation for this phenomenon but believed it to be the result of gas mixing and possible back-pressure(s). Despite the possible corrosive effect of CO_2 on the

Table 3. Summary of quantitative XRD analyses for the mineral standards

Incoming sample name	BGS Code	Mineralogy (%)				
		calcite	dolomite	siderite	quartz	hematite
GSR-12 Dolomite	MPLM701	nd	99.5	nd	0.5	nd
RC191/1 Calcite (Eire)	MPLM702	100	nd	nd	nd	nd
RC194/1 Calcite (Canada)	MPLM703	100	nd	nd	nd	nd
RC769/1 Siderite (Greenland)	MPLM704	nd	nd	97.1	0.8	2.1
Quartz	MPLM705	nd	nd	nd	100	nd

KEY
nd = not detected

Table 4. Summary of XRFS geochemical analysis for the mineral standards

Incoming sample name	BGS MPL code	SiO_2	TiO_2	Al_2O_3	Fe_2O_{3t}	Mn_3O_4	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	Cr_2O_3	SrO	ZrO_2	BaO	NiO	CuO	ZnO	PbO	LOI	Total
		%																				
GSR-12 Dolomite	MPLM701	0.62	0.02	0.10	0.20	0.01	21.76	30.02	0.03	0.04	<0.01	<0.1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
RC191/1 Calcite	MPLM702	0.03	<0.01	<0.01	<0.01	0.02	0.24	56.12	<0.05	<0.01	<0.01	<0.1	<0.01	0.03	<0.02	<0.02	<0.01	<0.01	<0.01	<0.01	43.32	99.76
RC194/1 Calcite	MPLM703	0.02	<0.01	<0.01	0.16	0.02	0.22	56.62	<0.05	<0.01	<0.01	<0.1	<0.01	0.06	<0.02	<0.02	<0.01	<0.01	<0.01	<0.01	43.93	101.03
RC769/1 Siderite	MPLM704	0.02	<0.02	<0.02	96.88	4.72	0.19	0.02	<0.06	<0.02	<0.02	<0.2	<0.02	<0.02	<0.03	<0.03	<0.02	<0.02	0.02	<0.02	26.90	101.85
Quartz	MPLM705	99.70	<0.01	0.02	0.14	<0.01	<0.05	<0.01	<0.05	<0.01	<0.01	<0.1	<0.01	<0.01	<0.02	<0.02	<0.01	<0.01	<0.01	<0.01	0.16	100.02

KEY
n/a = not available

delicate microthermobalance, Mettler's suggestion to run measurements with CO_2 as both the protective and reactive gas was used throughout this study. [Subsequent discussions with other users of the same instrument at Saint Gobain Gypsum, East Leake revealed that they had encountered similar problems when running with an N_2 protective gas and CO_2 reactive gas. The cause is still unknown].

For thermal analysis *c.*50 - 65 mg portions of each powdered sample were heated in 150 µl platinum crucibles from 30 to 1100˚C in a gas flow of 80 ml/minute CO_2 at a heating rate of 10˚C/minute.

In order to establish the lower detection limit of the different carbonate species, a series of mixtures of quartz with each carbonate species was prepared for TG-DTA analysis (Table 5). A total of 50 mg of each standard mixture was then accurately weighted into 150 µl platinum crucibles using a 5 decimal place Sartorius R200D balance.

Table 5. Summary mixtures of quartz and carbonate

Mixture no.	quartz		carbonate	
	%	mg	%	mg
1	98.000	49.000	2.000	1.000
2	99.000	49.500	1.000	0.500
3	99.500	49.750	0.500	0.250
4	99.800	49.900	0.200	0.100
5	99.900	49.950	0.100	0.050
6	99.950	49.975	0.050	0.025
7	99.980	49.990	0.020	0.010

The presence and quantification of the different carbonate species was determined by comparison with empirically-derived standard weight losses and temperatures (Table 2). However, in the case of the siderite standard RC769/1, TGA produced a weight loss of 27.70% (not 37.99% as shown by the equation in Table 2). Despite intensive research, no single, stoichiometric equation could be derived to explain this weight loss and it is therefore presumed to represent either incomplete reaction or the combination of two separate reactions. The standard siderite weight loss of 27.70% was used throughout this study.

3 Results of thermal analyses

3.1 MINERAL STANDARDS

The results of thermal analysis of the selected carbonate mineral standards are summarised in Table 6 and the labelled thermal analysis traces in Appendix 2.

The dolomite-bearing sample GSR-12 shows two major weight losses between *c.*730 and *c.*770ºC and between *c.*930 and *c.*960ºC which can both be ascribed to dolomite decomposition. Assuming that the dolomite has a close to end-member (non-ferroan) composition ($CaMg(CO_3)_2$), the dolomite concentration was calculated by comparison with the weight loss of a standard non-ferroan dolomite (47.73%, Table 2). The slight difference in weight loss between the two endothermic reactions suggests that the Mg:Ca ratio is not exactly 1:1 possibly caused by the substitution of Fe^{2+}, Mn^{2+}, Zn^{2+} or Ni^{2+} in the dolomite structure. A weak third endothermic effect between *c.*600 and *c.*650 ºC presents further evidence of some Fe^{2+} in the dolomite structure which is also confirmed by geochemistry data (Table 4).

The two calcite-bearing samples (RC191/1 and 194/1) show similar thermogravimetric profiles with a major, *c.*44% weight loss between *c.*950-987 ˚C. The weight loss suggests close-to-pure calcite contents of 99.73% (RC191/1) and 99.93% (RC194/1) respectively.

The siderite-bearing sample (RC769/1) produced a lower temperature weight loss between *c.*474 and 537 ˚C of *c.*27.7%, equivalent to *c.*97.4% siderite.

3.2 DETECTION LIMITS

Seven mixtures of each carbonate standard were run in 150 µl platinum crucibles from 30 to 1100˚C in a gas flow of 80 ml/minute CO_2 at a heating rate of 10˚C/minute. The results are summarised in Tables 7 to 10.

As shown by the tabulated data, TA confirms the presence of carbonate in the mineral mixtures and quantification suggests concentrations very close to those that were planned. Variation from the planned concentrations (generally <5%) is almost certainly due to errors inherent in the weighing and preparation of the mixtures. Larger errors were encountered for the siderite mixtures which may be due to the greater difficulty in separating and accurately weighing the iron-rich siderite particles which exhibit a mild magnetism and tend to form aggregates. The larger siderite errors may also possibly relate to the incomplete or dual reactions suggested in section 2.4.

In all cases the lowest carbonate concentration (0.020 %, 200 ppm) was detected and quantified. However, the detection of lower carbonate concentrations was precluded by the inability to accurately weigh samples of <0.01 mg using the 5 decimal place Sartorius R200D balance due to static effects between the mineral grains.

In order to determine the lowest detection limit for calcite in a composite sample using the TG-DTA technique, additional experiments were carried out using a Sartorius ME5 6-decimal figure balance.

Sample MPLM702 (Calcite RC191/1) was chosen as it showed the highest purity. The smallest, transferable quantities of calcite were weighed into a platinum crucible before adding between *c.*120 and *c.*160 mg quartz to produce calcite concentrations of *c.*0.01%, 100 ppm. The sample mixtures were then analysed as those previously. Sample details and results are shown in Table 9 (lower entries). An example TG curve for a low detection limit mixture is shown in Appendix 2.

Using such a technique, TG-DTA analyses successfully recorded a weight loss of $6.7291e^{-3}$ % which equates to an initial calcite weight of 0.015 % (150 ppm). Considering the size of the weight loss measured (Appendix 2), it would appear that the technique is capable of detecting lower calcite concentrations of perhaps 100 mg. However, proving this to be the case is precluded by handling/weighing difficulties.

Table 6. Summary of thermal analyses of mineral standards

Incoming sample name	BGS Code	Weight loss				Equivalent calcite content (%)	Equivalent dolomite content (%)	Equivalent siderite content (%)
		no.	temperature range (˚C)	%	attributed to			
GSR-12 Dolomite	MPLM701	1	*c*.611 – *c*.642	2.1278	dolomite decomposition 1		98.96	
		2	*c*.744 – *c*.769	21.1893	dolomite decomposition 2			
		3	*c*.933 – *c*.962	23.6167	dolomite decomposition 3			
RC191/1 Calcite	MPLM702	1	*c*.950 – *c*.987	43.8504	calcite decomposition	99.73		
RC194/1 Calcite	MPLM703	1	*c*.949 – *c*.987	43.9397	calcite decomposition	99.93		
RC769/1 Siderite	MPLM704	1	*c*.474 – *c*.537	27.7040	siderite decomposition			97.24

Table 7. Summary of thermal analysis of dolomite GSR-12 mixtures

Mixture no.	quartz (%)	dolomite (%)	Weight loss				Equivalent dolomite content (%)
			no.	temperature range (˚C)	%	attributed to	
1	98.000	2.000	1	*c*.601 – *c*.628	47.7829e^{-3}	dolomite decomposition 1	2.02
			2	*c*.738 – *c*.758	0.4136	dolomite decomposition 2	
			3	*c*.937 – *c*.945	0.5042	dolomite decomposition 3	
2	99.000	1.000	1	*c*.641 – *c*.657	12.3291e^{-3}	dolomite decomposition 1	0.71
			2	*c*.733 – *c*.753	0.1424	dolomite decomposition 2	
			3	*c*.937 – *c*.944	0.1820	dolomite decomposition 3	
3	99.500	0.500	1	*c*.737 – *c*.759	94.2459e^{-3}	dolomite decomposition 1	0.51
			2	*c*.934 – *c*.946	0.1477	dolomite decomposition 2	
4	99.800	0.200	1	*c*.738 – *c*.747	45.6772e^{-3}	dolomite decomposition 1	0.22
			2	*c*.937 – *c*.940	61.3174e^{-3}	dolomite decomposition 2	
5	99.900	0.100	1	*c*.732 – *c*.743	15.8691e^{-3}	dolomite decomposition 1	0.09
			2	*c*.935 – *c*.942	29.0146e^{-3}	dolomite decomposition 2	
6	99.950	0.050	1	*c*.735 – *c*.750	6.3248e^{-3}	dolomite decomposition 1	0.05
			2	*c*.939 – *c*.941	17.1661e^{-3}	dolomite decomposition 2	
7	99.980	0.020	1	*c*.730 – *c*.750	1.4801e^{-3}	dolomite decomposition 1	0.02
			2	*c*.937 – *c*.948	9.2926e^{-3}	dolomite decomposition 2	

Table 8. Summary of thermal analysis of calcite RC191/1 (Eire) mixtures

Mixture no.	quartz (%)	calcite (%)	Weight loss				Equivalent calcite content (%)
			no.	temperature range (˚C)	%	attributed to	
1	98.000	2.00	1	*c*.954 – *c*.965	0.9216	calcite decomposition	2.10
2	99.000	1.00	1	*c*.952 – *c*.964	0.4299	calcite decomposition	0.98
3	99.500	0.500	1	*c*.950 – *c*.962	0.2262	calcite decomposition	0.51
4	99.800	0.200	1	*c*.956 – *c*.961	77.0416e^{-3}	calcite decomposition	0.18
5	99.900	0.100	1	*c*.948 – *c*.959	61.8439e^{-3}	calcite decomposition	0.14
6	99.950	0.050	1	*c*.947 – *c*.959	19.4092e^{-3}	calcite decomposition	0.04
7	99.980	0.020	1	*c*.950 – *c*.955	9.9869e^{-3}	calcite decomposition	0.02

Table 9. Summary of thermal analysis of calcite RC194/1 (Canada) mixtures

Mixture no.	quartz (%)	calcite (%)	Weight loss				Equivalent calcite content (%)
			no.	temperature range (˚C)	%	attributed to	
1	98.000	2.000	1	*c*.948 – *c*.965	0.9010	calcite decomposition	2.05
2	99.000	1.000	1	*c*.949 – *c*.965	0.4809	calcite decomposition	1.09
3	99.500	0.500	1	*c*.947 – *c*.961	0.2140	calcite decomposition	0.49
4	99.800	0.200	1	*c*.949 – *c*.961	88.1119e^{-3}	calcite decomposition	0.20
5	99.900	0.100	1	*c*.948 – *c*.964	55.9616e^{-3}	calcite decomposition	0.13
6	99.950	0.050	1	*c*.949 – *c*.963	32.0740e^{-3}	calcite decomposition	0.07
7	99.980	0.020	1	*c*.945 – *c*.954	12.6495e^{-3}	calcite decomposition	0.03
8	99.0000	0.0090	1	*c*.940 – *c*.970	6.8588e^{-3}	calcite decomposition	0.016
9	99.0000	0.0160	1	*c*.940 – *c*.970	8.9111e^{-3}	calcite decomposition	0.020
10	99.5000	0.0090	1	*c*.940 – *c*.970	6.7291e^{-3}	calcite decomposition	0.015
11	99.8000	0.0120	1	*c*.940 – *c*.970	7.2632e^{-3}	calcite decomposition	0.017
12	99.9000	0.0120	1	*c*.940 – *c*.970	6.7902e^{-3}	calcite decomposition	0.015

Table 10. Summary of thermal analysis of siderite RC769/1 (Ivigtut, Greenland) mixtures

Mixture no.	quartz (%)	siderite (%)	Weight loss				Equivalent siderite content (%)
			no.	temperature range (˚C)	%	attributed to	
1	98.000	2.000	1	*c*.467 – *c*.503	0.5143	siderite decomposition	1.86
2	99.000	1.000	1	*c*.455 – *c*.493	0.2932	siderite decomposition	1.01
3	99.500	0.500	1	*c*.462 – *c*.500	0.1610	siderite decomposition	0.58
4	99.800	0.200	1	*c*.482 – *c*.501	58.5861e^{-3}	siderite decomposition	0.21
5	99.900	0.100	1	*c*.473 – *c*.499	42.1219e^{-3}	siderite decomposition	0.15
6	99.950	0.050	1	*c*.496 – *c*.508	9.6436e^{-3}	siderite decomposition	0.03
7	99.980	0.020	1	*c*.495 – *c*.510	419.6167e^{-6}	siderite decomposition	0.01

4 Conclusions

- The Mettler-Toledo SDTA851e thermal analysis system has been successfully installed and a BGS user manual has been written and working methodologies implemented.
- For the detection and quantification of low levels of carbonate species, combined TGA-DTA analysis offers significantly lower levels of detection than other mineralogical techniques such as X-ray diffraction analysis.
- TGA-DTA studies have measured concentration levels as low as 200 ppm (dolomite, siderite) and 150 ppm (calcite) in synthetic mixtures. Even lower detection limits are possible using this method but proving these is precluded by the difficulty of handling/weighing such small quantities.

5 Recommendations

- Users are advised to follow the protocols outlined in this report and the analysis programs setup. This report should be quoted when reporting data produced by the thermal analysis system.

References

British Geological Survey holds most of the references listed below, and copies may be obtained via the library service subject to copyright legislation (contact libuser@bgs.ac.uk for details). The library catalogue is available at: http://geolib.bgs.ac.uk.

BLOODWORTH, A.J., KEMP, S.J., INGLETHORPE, S.D.J. and MORGAN, D.J. 1987. Mineralogy and lithochemistry of strata beneath proposed low-level radioactive waste site at Bradwell, Essex; Report to Sir William Halcrow and Partners, Site Investigation Consultants. *British Geological Survey Technical Report* 87/13/C.

HAINES, P.J. 2002. *Principles of Thermal Analysis and Calorimetry*. In: HAINES P.J, editor. The Royal Society of Chemistry. 320p.

HARRISON, D.J., INGLETHORPE, S.D.J., Mitchell, C.J., KEMP, S.J., CHAODUMRONG, P. and CHARUSRIBANDHU, M. 1998. Procedures for the rapid assessment of limestone resources. *British Geological Survey Technical Report* WC/98/1.

HILL, J.O. 1991. *For Better Thermal Analysis and Calorimetry*. 3rd Ed., International Confederation for Thermal Analysis (ICTA), Newcastle, Australia.

HILLIER, S., SUZUKI, K. AND COTTER-HOWELLS, J. 2001. Quantitative determination of Cerussite (lead carbonate) by X-ray powder diffraction and inferences for lead speciation and transport in stream sediments from a former lead mining area of Scotland. *Applied Geochemistry*, 16, 597-608.

INGLETHORPE S.D.J. AND MORGAN D.J. 1993. Detection of ammonium in geological materials by evolved gas analysis. *Journal of Thermal Analysis*, 40, 29-40.

KEMP, S.J., INGLETHORPE, S.D.J. and WASPE, T.J. 1991. Bulk mineralogical data for samples from the Devonian of Dounreay BH1. *UK Nirex Core Characterisation Series Report* CC91D/030/IF-A-C.

MILODOWSKI A.E. AND MORGAN D.J. 1980. Identification and estimation of carbonate minerals at low-levels by evolved CO_2 analysis. *Nature*, 286, 248-249.

MILODOWSKI A.E. AND MORGAN D.J. 1984. Thermal-reactions of Leadhillite $Pb_4SO_4(CO_3)_2(OH)_2$. *Clay Minerals*, 19(5), 825-841.

MILODOWSKI A.E., MORGAN D.J., WARNE S.ST.J. 1989. Thermal-analysis studies of the dolomite-ferroan dolomite-ankerite series .2. Decomposition mechanism in flowing CO_2 atmosphere. *Thermochimica Acta*, 152(2), 279-297.

MORGAN D.J., 1977. Simultaneous DTA-EGA of minerals and natural mineral mixtures. *Journal of Thermal Analysis*, 12(2), 245-263.

MORGAN D.J., WARNE S.ST.J., WARRINGTON, S.B. AND NANCARROW, P.H.A. 1986. Thermal-decomposition reactions of caledonite and their products. *Mineralogical Magazine*, 50, 357, 521-526.

MORGAN D.J., WARRINGTON, S.B AND WARNE S.ST.J. 1988a. Earth sciences applications of evolved gas-analysis - a review. *Thermochimica Acta*, 135, 207-212.

MORGAN D.J., MILODOWSKI A.E., WARNE S.ST.J., WARRINGTON, S.B. 1988b. Atmosphere dependence of the thermal-decomposition of manganite, gamma-MnO.OH. *Thermochimica Acta*, 135, 273-277.

PARSONS A.J., INGLETHORPE S.D.J., MORGAN D.J., AND DUNHAM, A.C. 1997. Evolved gas analysis (EGA) of brick clays, *Journal of Thermal Analysis* 48(1), 49-62.

SNYDER, R.L. AND BISH, D.L. 1989. Quantitative analysis. In: Bish, D.L., Post, J.E. (Eds), *Modern Powder Diffraction*, *Reviews in Mineralogy*, Volume 20, Mineralogical Society of America, USA, pp. 101-144 (Chapter 5).

WARNE S.ST.J., BLOODWORTH, A.J. AND MORGAN D.J. 1985. Thermomagnetometry and evolved gas-analysis in the identification of organic and pyritic sulfur in coal and oil-shale. *Thermochimica Acta***,** 93**,** 745-748**.**

WARNE S.ST.J. 1986. Applications of variable atmosphere DTA (in CO2) to improved detection and content evaluation of anhydrous carbonates in mixtures. *Thermochimica Acta***,** 109**,** 243-252**.**

Appendix 1 BGS methodology

OPERATING INSTRUCTIONS
FOR THE
METTLER-TOLEDO SDTA851^{e}
THERMAL ANALYSIS SYSTEM
(ROOM P029)

1 RESTING CONDITIONS

The TGA/SDTA851^e should be permanently left on and the balance constantly purged with N_2 as a protective gas (*c*. 10cm^3/min on flowmeter). [CO_2 may also be used as a protective gas for a short time period where CO_2 is to be used as reactive gas, to avoid an unexpected low temperature weight gain].

Check the recirculating cooling agent (22ºC) on a regular basis for water level and contamination. If the water level has dropped, top-up as necessary. If the coolant shows any cloudiness, drain the fluid and replace using the correct dilution ratio. Also check that the water flow is maintained using the red flow-wheel indicator.

2 PREPARATION (DAY BEFORE ANALYSIS)

2.1 Ensure TGA/SDTA851^e is switched on. [The mains switch (red) is located towards the top of the rear panel of the module.]

2.2 Switch on the PC and log on to the AD domain.

2.3 Double-click on the *STAR^e software program* icon on the desktop.

Note: If an error message appears, refer to Appendix M1 for guidance.

2.4 Enter username (METTLER) and password (↵)

2.5 Check that adequate supplies of N_2 and/or CO_2 gases are available in the cylinder store (DP407 in P-U block quadrangle) and open relevant regulators.

2.6 In P029, gradually turn on the gas supply at the relevant gas tap (CO_2 or N_2) making sure that the gas pressure indicated on the inline pressure gauge does not exceed 0.8 bar.

2.7 On the TGA/SDTA851^e control panel, depress the 'Rotate' button until 'Gas1 and 'Gas2' appear on LCD display. Then, also on the TGA/SDTA851^e control panel, depress the gas button (2 gas cylinder symbols, labelled '1' and '2') to indicate the reactive gas flow rate. Note that by default, 'Gas 1' indicates N_2 and 'Gas2' indicates CO_2.

2.8 On the gas flow control unit (TS0800GC1) beside the TGA/SDTA851^e, turn the knob 1 (N_2) or 2 (CO_2) respectively to adjust the reactive gas flow to 80ml/min (shown on the TGA/SDTA851^e control panel). Make sure that the protective gas (N_2or CO_2) flows at ~10cm^3/min on the flowmeter, adjusting using the knob on the flowmeter itself.

2.9 Leave the gas(es) switched on overnight to settle and purge the TGA/SDTA851^e.

3 CALIBRATION AND ADJUSTMENT

3.1 Before each batch of samples, perform a calibration check using the supplied In/Al metal standards.

3.2 From within the *STAR*^{e} software, click on the *'Routine editor'*.

3.3 From the *'Method'* drop down menu, select *'Select'* - *'Check TGA851 In/Al'*.

3.4 Place an alumina crucible containing the prepared In/Al mixture in position 34 on the carousel. ***Note:*** *The In/Al standard can be re-used for future calibrations.*

3.5 Fill in the weight of pre-prepared In/Al (taking details from the sheet pinned to notice board in P029), add the sample name 'In/Al check' and sample position '134'.

3.6 Click *'Send Experiment'*.

3.7 To evaluate whether the In/Al check is within specification, open the Evaluation Window by minimising the Module Control Window.

3.8 From the *'Functions'* drop down menu, select *'Evaluation Window'*.

3.9 From the *'File'* drop down menu, select *'Open'* and then *'Evaluation'*. Select the relevant In/Al check and follow the instructions that appear in the window.

3.10 The In/Al check is evaluated automatically. If the values are within specification, the following text appears: *'The Module is within specifications!'*. If the values are not within specification, the following text appears: *'Please adjust the TGA/SDTA851*^{e}*!'*.

3.11 If the results of the check are not within specification, repeat the experiment with new standard materials. If the results are still not within specification, carry out a total adjustment (see Appendix M2).

4 SAMPLE ANALYSIS

4.1 From within the *STAR^{e}* software, click on the *'Routine editor'*.

4.2 From the *'Method'* drop down menu, select *'Select'* and choose the relevant method from the options displayed in the window.

4.3 On the Sartorius 5-figure balance, weigh a clean crucible of correct material for analysis (platinum, aluminium, ceramic etc), zero the balance and weigh sample material (usually c.50mg) into the crucible. Record the sample weight.

4.4 In the software window, fill in the sample name, sample weight and sample position in the carousel. [The first sample position on the sample carousel is 101.]

4.5 Note: When carrying out experiments involving temperatures above 1100°C and platinum crucibles, make sure that a sapphire disk is placed on the sample holder arm before analysis!

4.6 Click *'Send Experiment'*.

5 EVALUATION

5.1 From the main *STAR^{e}* software window, click '*Functions*' drop down menu and select the '*Evaluation window*'. In the new window from the 'File' drop down menu, select '*Open curve*'. Select the required sample curve and click '*Open*'.

5.2 To additionally display the DTG curve, select '*Math*' and '*1st derivative*'.

5.3 To additionally display the DTA curve, select '*TA*' and '*SDTA*'.

5.4 To calculate weight losses, click on the original curve (always remember to click on the curve you want to work on) and draw a window over the area of the weight loss. Select '*TA*' and '*Step Horiz.*' or '*Step Tang.*' Values for weight loss in % and g will appear adjacent to the curve.

5.5 When calculations/graphical manipulation complete, click the '*File*' drop down menu and select '*Save evaluation*'. Fill in appropriate file name, using MPL code.

5.6 To export an evaluation for reporting purposes, click the ‘*File*‘ drop down menu and select ‘*Import/Export*’ and ‘*Export other format*’ (e.g. *.emf, *.tif, *.txt).

6 TERMINATING THE STAR^{e} SOFTWARE AND SHUT-DOWN

6.1 In Evaluation window, click the ‘*File*‘ drop down menu and select ‘*Exit*’.

6.2 From the main *STAR*^{e} software window, click ‘*System*’ drop down menu and select the ‘*Exit*’. Shut down PC as usual.

6.3 Turn back gas flow of Nitrogen until *c.*10cm^3/min is shown on the flow-meter. In case of CO_2 usage, turn off gas at the gas tap in P029 and via the regulator and cylinder in DP407.

APPENDIX M1. Error message while logging into the STARe software.

This procedure is necessary if an error message is received when attempting to start the STARe software system. This procedure restarts the INGRES database.

1.1 Log off AD domain.

1.2 Log in as *‘KWP19767 (this computer)*’.

1.3 Enter username *‘INGRES’* and password *‘weiqing1’*.

1.4 From the Start Menu, select ‘*Control Panel*’.

1.5 Select ‘*Administrative Tools*’ and then ‘*Services*’.

1.6 Select ’*Ingres intelligent database [II]*’ from the list.

1.7 Within the new window, select the ’*log on*’ tab.

1.8 Fill in the log in name ’*.\ingres*’ and password ‘*weiqing1*’ and click the ’*Apply*’ button.

1.10 A window ‘*The account .\ingres has been granted the Log On As A Service right*’ will appear. Click ‘*OK*’ button.

1.11 On the ‘*General*’ tab, click the ‘*Start*’ button. A window will appear advising that ‘*Windows is attempting to start the Ingres Intelligent Database II*’. Click ‘*OK*’.

1.12 Close all windows and log off.

1.13 log on AD domain as per usual.

APPENDIX M2 Total adjustment.

This procedure is necessary if the results of the In/Al calibration check are outside specification.

1.1 From within the *STAR^e* software, click on the *'Routine editor'* and select '*Total adjustment*'.

1.2 Prepare the sample for the experiment by following the instructions in text box. An alumina crucible with In/Al total is already placed on the carousel on position 131 which can be re-used. The weight for this pre-prepared standard is shown on the sheet on the notice board in P029.

1.3 Fill in sample name '*In/Al total*', the sample weight (from details on the notice board) and sample position '*131*'.

1.4 Click *'Send Experiment'*.

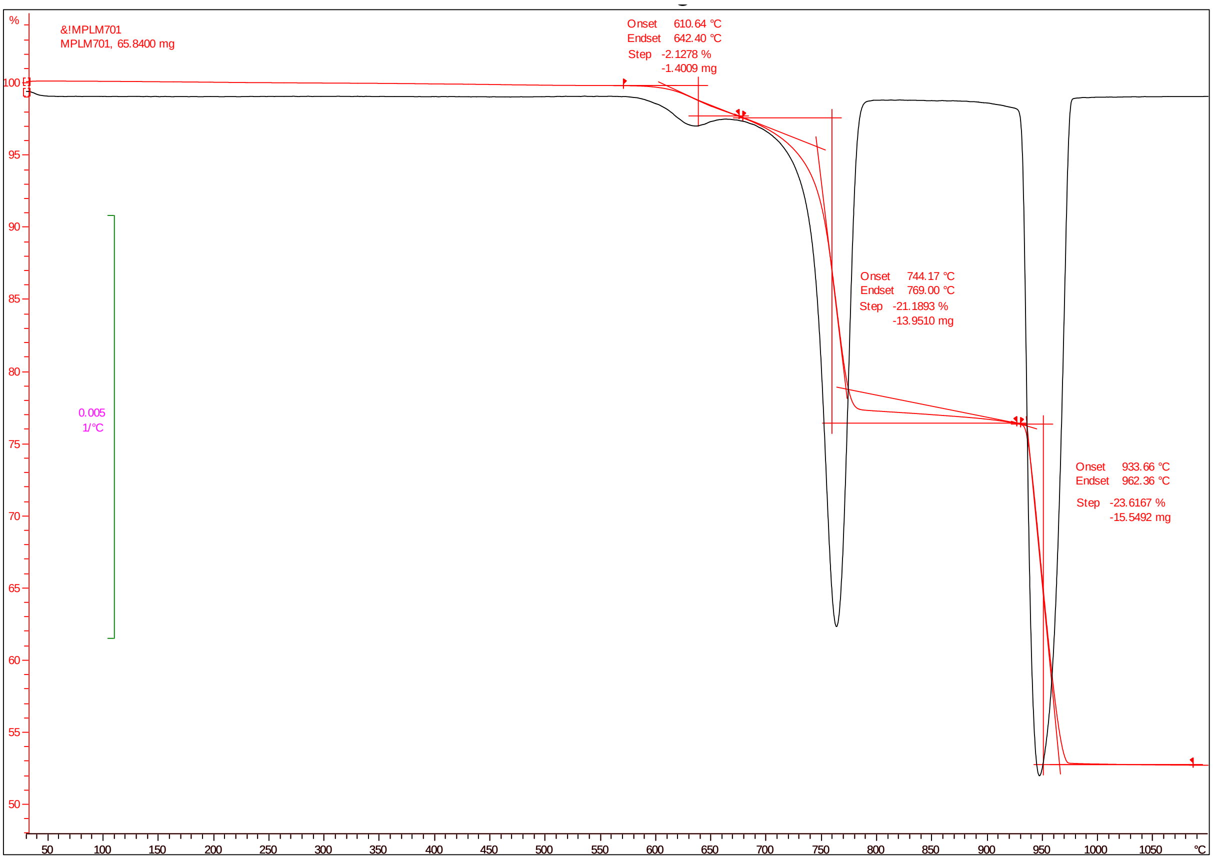
1.5 After completion of the experiment, an information box will appear with the new calibration values. Click '*OK*' button to accept these new values.

1.6 Perform another In/Al check (Section 3) to see if the values are now within limits.

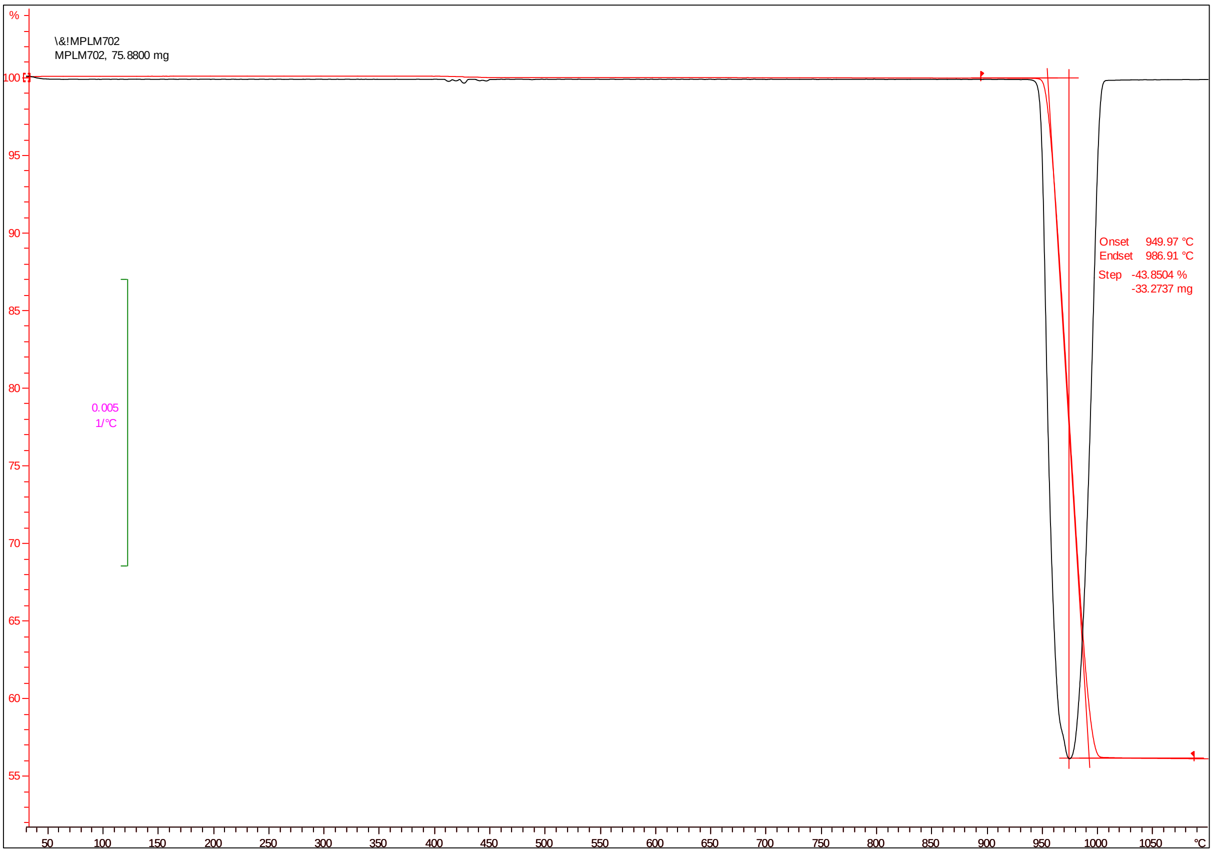
Appendix 2 Thermal analysis traces for the carbonate mineral standards and low detection limit mixture

[TG traces are shown in red, DTG traces are shown in black except for low detection limit sample where only the TG trace isshown]

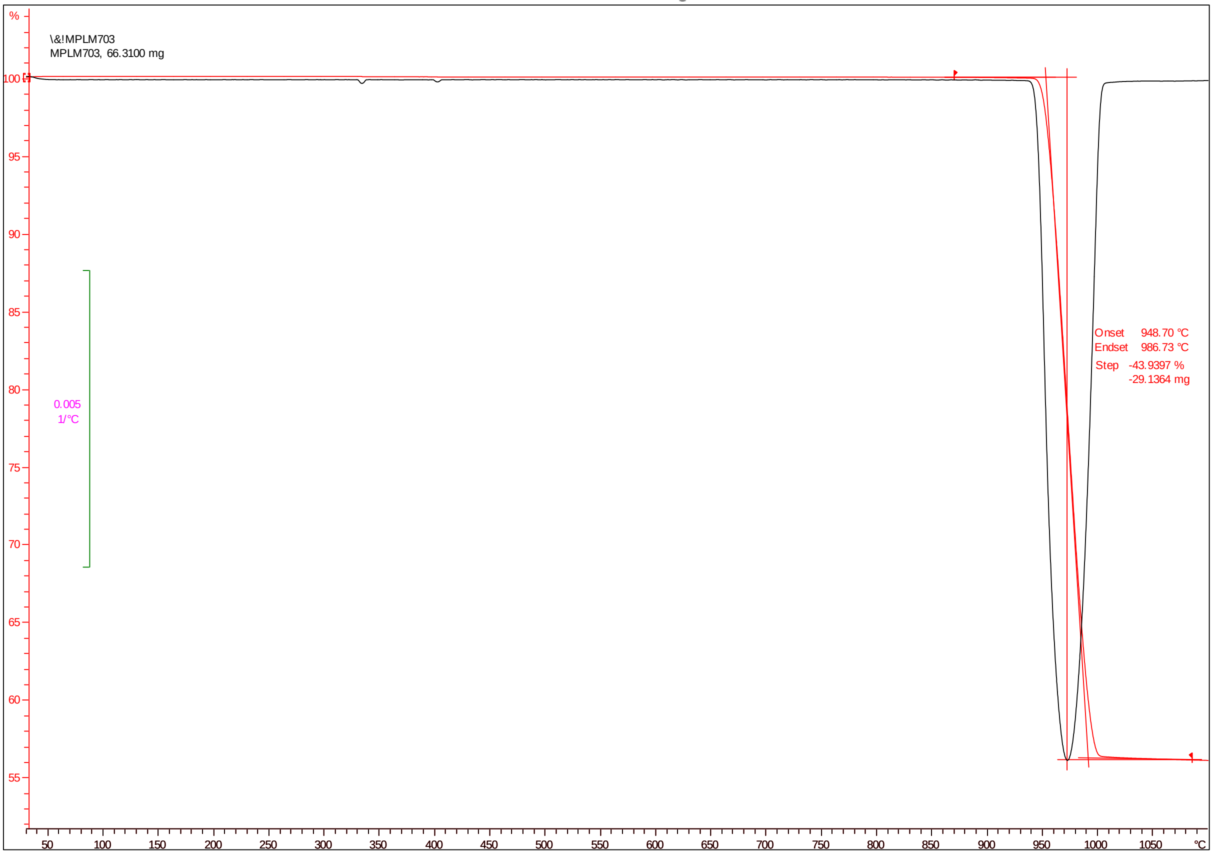
GSR-12 Dolomite, MPLM701



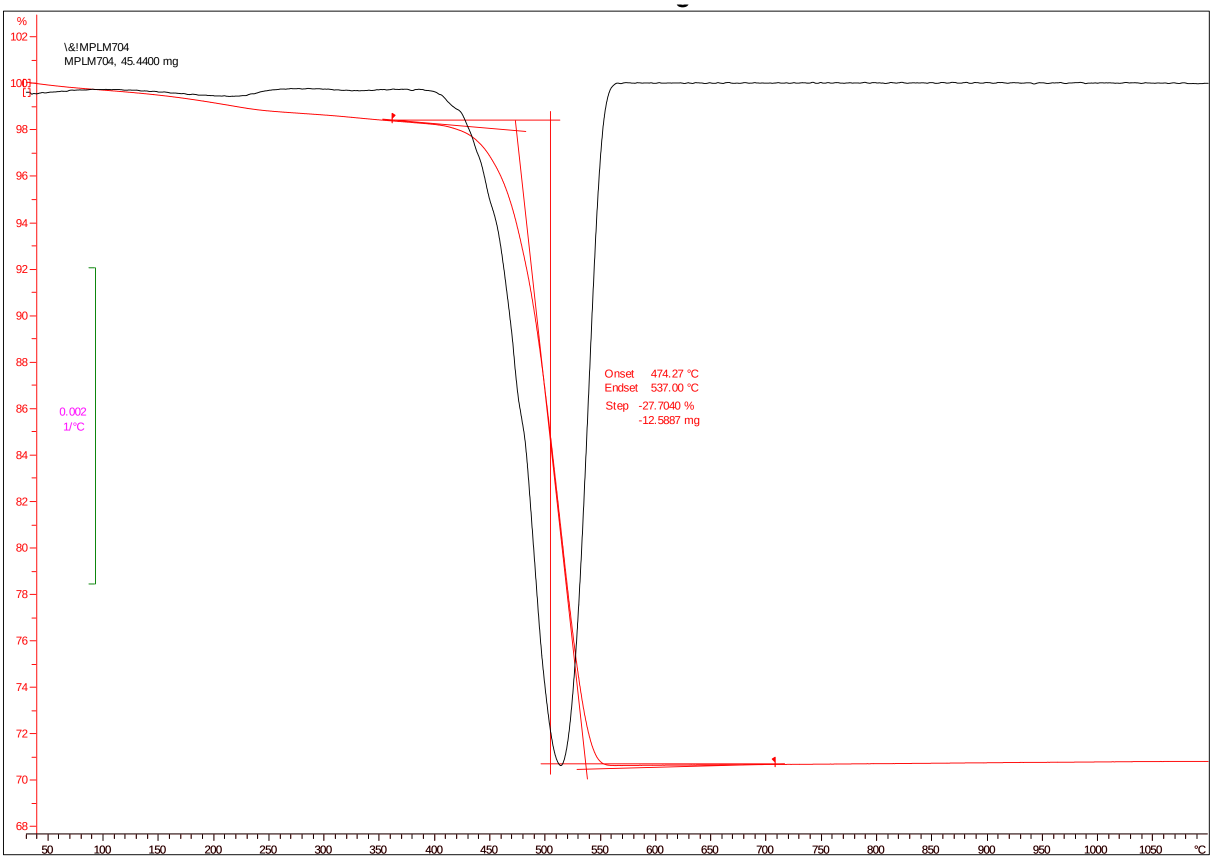
RC191/1 Calcite (Eire), MPLM702



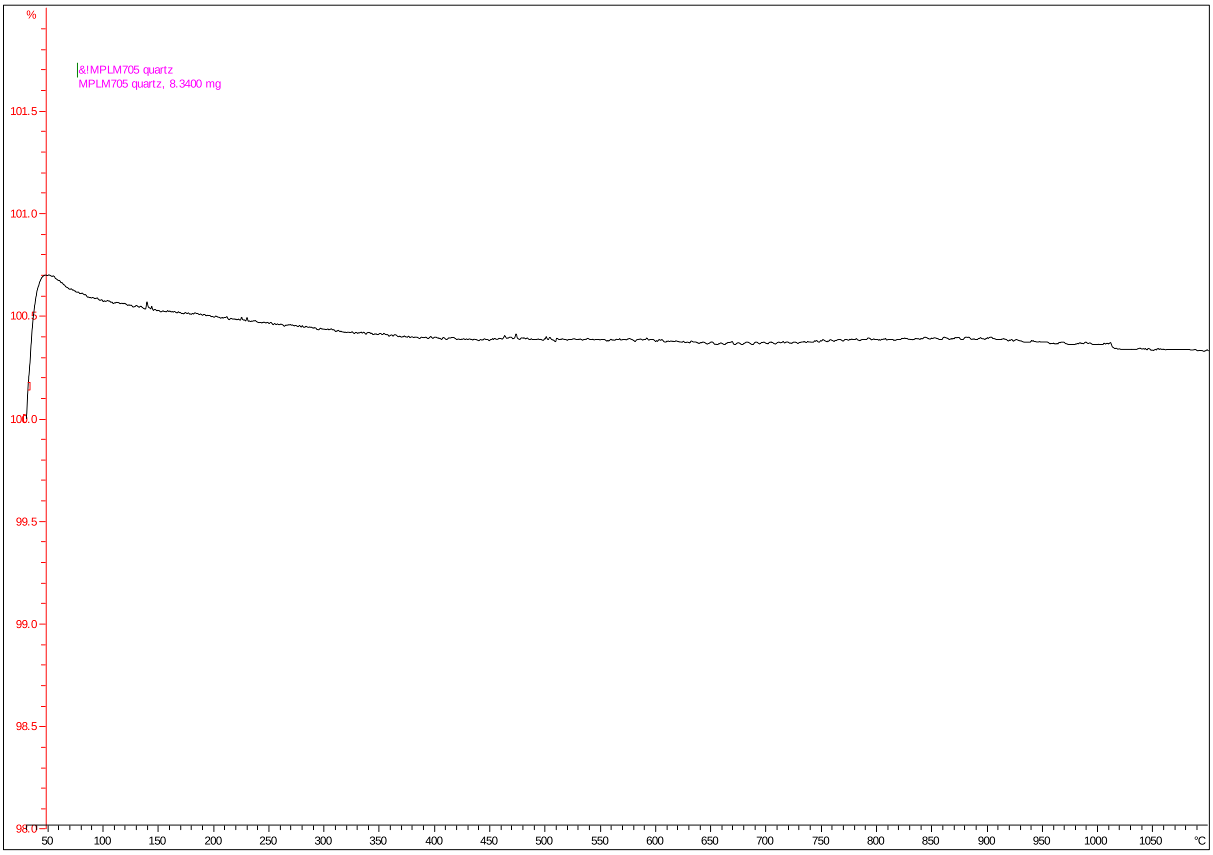
RC194/1 Calcite (Canada), MPLM703



RC769/1 Siderite (Greenland), MPLM704



Quartz, MPLM705



Low detection limit mixture: 99.991% quartz, 0.009% calcite