Bulk chemical composition of samples recovered from asteroid Ryugu — Analysis of extraterrestrial material by WDXRF and TG-MS —

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Abstract

Spacecraft HAYABUSA2 successfully collected a 5.4 g sample from the surface of asteroid Ryugu that was returned to Earth on Dec. 6, 2020. Analysis of the asteroid Ryugu sample was performed using a ZSX Primus IV wavelength dispersive X-ray spectrometer and a Thermo plus EVO2 TG-DTA8122 thermogravimetric differential thermal analyzer coupled with GC-MS (TG-MS).

A very small (24 mg) Ryugu sample (C0108) was analyzed by XRF in powder form without any pelletization or thin film covering. Analytical results by the fundamental parameter (FP) method for 23 elements including carbon and oxygen were consistent with the values from other analytical methods. Elemental abundance in Ryugu shows close similarity with the abundance determined for the CI chondrite meteorite, whose composition is the most primitive and similar to solar system elemental abundance.

About 1 mg of Ryugu sample grain A0040 was used for the TG-MS measurement. Total H_2O and CO_2 content of the Ryugu sample were 6.8 and 5.5 mass%, respectively. The Ryugu sample contains less H_2O than CI chondrite does. The TG-MS measurement reveals differences in H_2O release behavior at low temperature (<300°C) between Ryugu and CI chondrite.

1. Introduction

Spacecraft Hayabusa2, which launched in 2014, made two touchdowns on asteroid Ryugu during 2019 and collected surface materials. The sample capsule was returned to Earth on Dec. 6, 2020. The total sample amount collected from Ryugu was 5.4 g.

Samples recovered from asteroid Ryugu are extraterrestrial material directly obtained in outer space. Since they were delivered to Earth without any alteration or contamination by terrestrial materials, there are essential differences between the Ryugu sample and any meteorites recovered on the earth, even though both originated in outer space. It is expected that the analytical results of such a unique material by state-of-the-art methods will produce new discoveries and contribute to solar system sciences.

After a curation process in JAXA (Japanese Aerospace Exploration Agency) for six months, initial analysis of Ryugu samples were performed between June 2021 and May 2022. Rigaku was joined XRF group in the Initial Analysis Chemistry Team, which is one of six teams, chemistry, stony materials, sandy materials, volatiles, organic macromolecule and soluble organic matter team, of initial analysis project and performed bulk chemical analysis using wavelength dispersive X-ray fluorescence (WDXRF).

As XRF has the advantage of being a non-destructive analytical method, the mission of the XRF group in the Initial Analysis Chemistry Team was firstly to determine the bulk chemical composition of the Ryugu sample prior to other chemical analysis, and to hand over the compositional data and whole samples to other analysis groups. XRF analyses were performed using WDXRF, energy dispersive XRF (EDXRF) and synchrotron radiation XRF (SRXRF)(1). WDXRF analyzed bulk composition including carbon and oxygen. To determine the carbon dioxide and water content in the Ryugu sample by another analytical method, thermal analysis was also performed by TG-MS.

2. X-ray Fluorescence Analysis

2.1 Instruments

It was specified that the samples for XRF measurements were to be used as-is, in powdered form, so the entire sample could be recovered after XRF analysis and used for other measurement techniques. For this reason, the pressed pellet technique was not used as a sample preparation method. Carbon cannot be determined by WDXRF in the presence of polymer thin film, which is typically used to prevent particles from spilling from the sample holder during vacuum, leak and measurement sequences. Therefore, a Rigaku ZSX Primus IV system was used. It is a sequential spectrometer that can analyze carbon and is equipped with tube-above optics to eliminate the risk of any sample spilling during measurements.

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Fig. 1. ZSX Primus IV spectrometer.

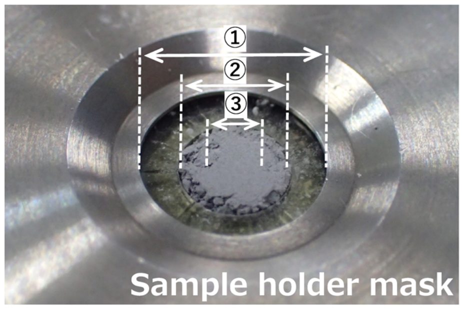

Fig. 2. Size in sample measurement.
①: Diameter of sample holder mask (10 mm), ②: Diameter of sample cell (6 mm), ③: Diameter of measurement (3 mm), Powder sample in image is just a test sample.

A new vacuum system was developed as a specialized function for ZSX Primus IV for the Ryugu sample analysis to avoid scattering of non-pelletized powder sample particles in the spectrometer's sample chamber during the vacuum and leak measurement sequences. Furthermore, the sample transport system was optimized to prevent particles from moving during transportation sequences. Vacuum pumps were replaced with scroll-type dry pumps. The ZSX Primus IV system for the Ryugu sample analysis was installed in a clean room at Rigaku's Osaka factory when the actual analysis was performed.

2.2 Analytical method

Asteroid Ryugu is classified as a C-type asteroid because spectroscopic observation revealed that it contains hydrous minerals and carbon. Ryugu is mainly composed of silicate minerals, and its bulk chemical composition is considered to be similar to the composition of Ivuna-type CI chondrite meteorites in the carbonaceous chondrites group[2]. As there is no reference material similar to the bulk compositions of carbonaceous chondrites [e.g. (3)] in commercially available geological reference materials, it would be necessary to add reference samples that are not matrix-matched to expand the range of composition in the equipment calibration. Therefore, the fundamental parameter (FP) method was used as a quantification method instead of the conventional empirical calibration method, which requires reference materials matrix-matched with unknown samples in the quantification.

Measured components in the Ryugu sample consisted of 23 elements (C, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Rb and Zr), which ranges from major to trace components. Spectroscopic observation indicates the asteroid Ryugu contains H_2O[2] and the H_2O content is estimated to be a maximum of 20 mass%. In the analysis using the FP method, quantification of total oxygen in the Ryugu sample was investigated to consider the influences of H_2O content in theoretical calculations in the FP method without direct determination of H_2O content by any method.

FP calibration curves were established by using 50 reference materials mainly composed of silicate rock, additional ore standards and so on. Ferroalloy standards were used for FP calibration of carbon and pure reagents of oxide material were used for FP calibration of oxygen.

2.3 Samples and sample preparation

Analysis was performed for Ryugu sample No. C0108 provided by JAXA. The sample was carefully ground using a quartz pestle in a quartz vial and poured into the center hole of a sample cell with 6 mm diameter and 0.6 mm depth[1, 5]. The powder sample was softly compacted in the sample cell using an acrylic plate to make the surface flat for measurement. The mass of the sample on the sample cell was 24 mg. The sample cell was placed in a standard ZSX Primus IV sample holder with 10 mm mask (Figure 2). All reference powder samples (c.a. 30 mg) were loaded into the above sample cell in the same manner.

2.4 Measurement conditions

Measurements were performed with a 3 kW X-ray tube load. Current and voltage were optimized for each measurement line. Primary X-ray filters were used for all measurements to reduce any sample damage during measurement. A 3 mm collimator mask was applied to measure the Ryugu sample. To analyze carbon with high accuracy, the Auto Pressure Control (APC) function was used and constant vacuum (13 Pa) was maintained during measurement. Measurement conditions are shown in Table 1.

2.5 Analytical results

2.5.1 Evaluation of analytical method

To evaluate the new application for the asteroid sample analysis using the FP method, test samples, whose chemical compositions were known were analyzed. Five test samples were prepared as follows: two meteorites of carbonaceous chondrite (Murchison meteorite), serpentinite, soil, laterite and bauxite. These samples are mainly composed of silicate minerals and

Table 1. Measurement conditions.

Component	Measurement line	kV-mA	Primary beam filter	Slit	Analyzing crystal	Detector	Measurement time (sec)		
							Peak	Back ground1	Back ground2
C	C-KA	30–100	Be	S8	RX61	PC	100	50	50
O	O-KA	30–100	Be	S4	RX35	PC	40	10	10
Na	Na-KA	30–100	Be	S4	RX35	PC	40	10	
Mg	Mg-KA	30–100	Be	S4	RX35	PC	20	5	
Al	Al-KA	30–100	Be	S4	PETH	PC	20	5	
Si	Si-KA	30–100	Be	S4	RX4	PC	20	5	
P	P-KA	30–100	Be	S4	RX9	PC	40	10	
S	S-KA	30–100	Be	S4	RX9	PC	20	5	
Cl	Cl-KA	30–100	Be	S2	RX9	PC	40	10	
K	K-KA	40- 75	Al	S4	LiF(200)	PC	40	10	
Ca	Ca-KA	40- 75	Al	S4	LiF(200)	PC	20	5	
Ti	Ti-KA	40- 75	Al	S2	LiF(200)	SC	40	10	
V	V-KA	50- 60	Al	S2	LiF(200)	SC	40	10	
Cr	Cr-KA	50- 60	Al	S2	LiF(200)	SC	20	5	
Mn	Mn-KA	50- 60	Al	S2	LiF(200)	SC	20	5	
Fe	Fe-KA	60- 50	Al	S2	LiF(200)	SC	20	5	
Co	Co-KA	60- 50	Al	S2	LiF(200)	SC	40	10	10
Ni	Ni-KA	60- 50	Al	S2	LiF(200)	SC	20	5	
Cu	Cu-KA	60- 50	Al	S4	LiF(200)	SC	40	10	
Zn	Zn-KA	60- 50	Al	S4	LiF(200)	SC	40	10	
Rb	Rb-KA	60- 50	Ni	S4	LiF(200)	SC	40	10	10
Sr	Sr-KA	60- 50	Ni	S4	LiF(200)	SC	40	10	10
Zr	Zr-KA	60- 50	Ni	S2	LiF(200)	SC	40	10	10

contain H_2O or H_2O and carbon. The value of oxygen content is reported for the Murchison meteorite[(6)].

Analytical results for test samples are shown in Table 2. The table also shows chemical composition values reported in literature or certificates for test samples. The results including carbon by WDXRF are consistent with chemical values. Since analysis results show good agreement with the chemical values, even though the content of H_2O in these samples exhibits wide variation, it indicates that a determination of total oxygen content is effective in analysis for bulk composition of samples containing H_2O.

2.5.2 Bulk compositions of Ryugu sample

Figure 3 shows an image of the Ryugu sample from a built-in camera during measurement. Results of the analysis are shown in Table 3. Chemical composition by WDXRF is quite consistent with the results by ICP-MS[(1)] (Figure 4). Carbon content shows agreement with the values by EMIA-step and TG-MS (4.63–3.8 mass%)[(1)].

Bulk composition of the Ryugu sample is compared with the CI chondrite meteorite[(3)], whose elemental abundances shows close similarity to solar system abundance except for H, Li, C, N, O and noble gas and is considered the most pristine among the other carbonaceous chondrite meteorites (Figure 5).

Elemental abundances of Ryugu and CI chondrite are similar in the wide elemental range from light to heavy elements. Total oxygen content in the Ryugu sample shows depletion compared to CI chondrite. The depletion in oxygen content is consistent with the low O/Si ratio determined by negative muon analysis of the Ryugu sample[(7)].

3. Thermal Analysis

3.1 Instruments

The major aim of thermal analysis is to analyze evolution of H_2O in the Ryugu sample. Thermogravimetry-differential thermal analysis / gas chromatograph mass spectrometry system (TG-DTA/GC-MS; TG-MS), which can detect other evolved gases as well as H_2O, was used for Ryugu sample analysis. This system can quantify evolved gases and provide their thermal profiles, which show the MS signal as a function of temperature.

Figure 6 shows an image of the instrument used for Ryugu sample analysis. Sample measurements were performed by a hyphenated system, Rigaku Thermo plus EVO2 TG-DTA8122 connected to JEOL JMS-Q1500GC by 1ch. MS interface.

3.2 Samples

Samples provided for thermal analysis were Ryugu sample A0040 and Ivuna meteorite (CI carbonaceous chondrite). The masses of the Ryugu and Ivuna samples were 0.977 mg and 0.912 mg, respectively. The total mass of the samples was used for the measurements.

Figure 7 shows sample observation images before

Table 2. Analytical results of test samples.

(mass%)

Components	Carbonaceous chondrite: Murchison meteorite					sepentinite: SARM47			soil: JSO-1		
	Chemical values(6)	XRF values	Standard deviation	XRF values	1σ	Certified values	XRF values	1σ	Certified values	XRF values	1σ
C	2.2	2.0	0.0499	1.7	0.0536		0.1	0.0278	*8.91*	8.6	0.0991
O	43.05	43.5	0.2905	43.1	0.2907		53.0	0.1994		50.8	0.2540
Na	0.39	0.242	0.0102	0.226	0.0103	*0.037*	0.0151	0.0062	0.497	0.292	0.0093
Mg	11.5	12.1	0.0681	12.4	0.0683	25.38	25.8	0.1071	1.27	0.914	0.0125
Al	1.13	1.22	0.0139	1.14	0.0146	0.577	0.589	0.0090	9.56	9.94	0.0588
Si	12.7	12.5	0.0737	12.9	0.0724	16.96	17.1	0.1022	17.9	17.9	0.0958
P	0.103	0.0904	0.0012	0.0832	0.0013	*0.009*	0.0034	0.0002	0.209	0.210	0.0023
S	2.7	2.66	0.0186	2.38	0.0204	*0.02*	0.0410	0.0012	0.2	0.172	0.0028
Cl	0.043	0.0256	0.0015	0.0333	0.0014		0.0101	0.0011		0.0170	0.0013
K	0.037	0.0339	0.0017	0.0366	0.0019	*0.017*	0.0091	0.0008	0.282	0.263	0.0053
Ca	1.29	1.36	0.0179	1.32	0.0180	0.07	0.0600	0.0028	1.82	1.92	0.0239
Ti	0.055	0.0669	0.0042	0.0683	0.0042	0.006	0.0065	0.0028	0.737	0.797	0.0149
V	0.0075	0.0063	0.0016	0.0059	0.0015				0.0300	0.0397	0.0024
Cr	0.305	0.400	0.0076	0.377	0.0079	0.2	0.232	0.0057	*0.0071*	0.0100	0.0019
Mn	0.165	0.196	0.0043	0.196	0.0045	0.046	0.0440	0.0018	0.160	0.158	0.0040
Fe	21.3	22.2	0.1652	22.7	0.1632	2.9	2.81	0.0261	7.96	7.93	0.0725
Co	0.056	0.0640	0.0019	0.0663	0.0019	0.0079	0.0083	0.0006	*0.0032*	0.0046	0.0008
Ni	1.23	1.27	0.0066	1.28	0.0063	0.2221	0.215	0.0032	*0.0039*	0.0010	0.0009
Cu	0.013	0.0145	0.0007	0.0145	0.0006	*0.0005*	0.0007	0.0003	*0.0169*	0.0166	0.0006
Zn	0.018	0.0191	0.0006	0.0202	0.0006	0.0045	0.0047	0.0003	*0.0105*	0.0109	0.0005
Rb	0.00016	0.0002	0.0002		0.0002				*0.0015*	0.0020	0.0002
Sr	0.001	0.0015	0.0002	0.001	0.0002	*0.0003*	0.0002	0.0001	*0.0196*	0.0179	0.0004
Zr	0.0007	0.0001	0.0002		0.0002				*0.0096*	0.0085	0.0003
H_2O							12.5		*7.88*		

Components	laterite: ITAK212			bauxite: BCS395		
	Certified values	XRF values	1σ	Certified values	XRF values	1σ
C		0.7	0.0323			
O		43.7	0.2726		60.4	0.1970
Na					0.0330	0.0054
Mg	0.778	0.614	0.0108	0.01	0.200	0.0060
Al	4.64	4.01	0.0302	27.7	27.0	0.1248
Si	8.01	7.00	0.0418	0.579	0.523	0.0093
P	0.0061	0.0055	0.0003		0.0499	0.0008
S		0.0450	0.0012		0.0490	0.0012
Cl		0.0050	0.0010		0.0049	0.0009
K		0.0081	0.0012		0.0139	0.0011
Ca	0.0197	0.0200	0.0018	0.036	0.0300	0.0025
Ti	0.135	0.137	0.0048	1.16	1.17	0.0163
V		0.0437	0.0022		0.0331	0.0019
Cr	3.08	2.69	0.0263	*0.0453*	0.0488	0.0027
Mn	0.738	0.906	0.0118	*0.0042*	0.0070	0.0011
Fe	40.02	39.3	0.2117	11.4	10.4	0.0824
Co	0.1333	0.122	0.0027		0.0008	0.0007
Ni	0.697	0.665	0.0062	*0.0034*	0.0025	0.0007
Cu	0.1387	0.123	0.0014	*0.0021*	0.0018	0.0004
Zn		0.0273	0.0009	*0.0043*	0.0038	0.0004
Rb		0.0002	0.0003		0.0001	0.0001
Sr		0.0001	0.0002	*0.0023*	0.0025	0.0002
Zr		0.0004	0.0003		0.0385	0.0006
H_2O		6			28	

H_2O content was measured by TG-MS except for JSO-1

Itaric is reference value

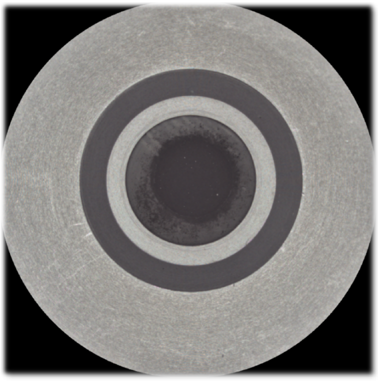

Fig. 3. Ryugu sample at the measurement. Image was taken inside the sample chamber of ZSX Primus IV.

Table 3. Analytical results of Ryugu sample.

(mass%)

Component	Ryugu	
	XRF values	1σ
C	4.6	0.0750
O	39.9	0.2871
Na	0.799	0.0150
Mg	12.9	0.0661
Al	1.04	0.0123
Si	13.1	0.0703
P	0.106	0.0014
S	5.03	0.0323
Cl	0.0784	0.0021
K	0.0584	0.0023
Ca	1.46	0.0187
Ti	0.0502	0.0035
V	0.0064	0.0013
Cr	0.348	0.0071
Mn	0.259	0.0051
Fe	18.9	0.1384
Co	0.0605	0.0017
Ni	1.16	0.0057
Cu	0.0112	0.0005
Zn	0.0346	0.0006
Rb	0.0004	0.0002
Sr	0.0012	0.0002
Zr	0.0003	0.0002

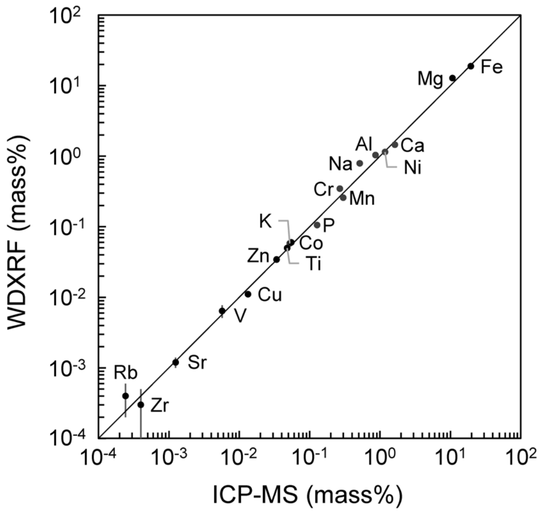

Fig. 4. XRF values compared with ICP-MS[1]. Error bar: 1σ.

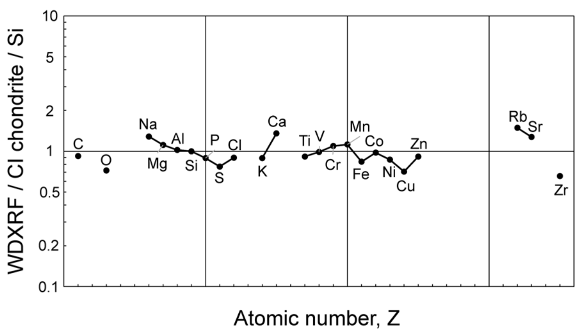

Fig. 5. Elemental abundances of Ryugu sample and CI chondrite meteorite[3].
The ratio of CI chondrite to Ryugu sample normalized by Si.

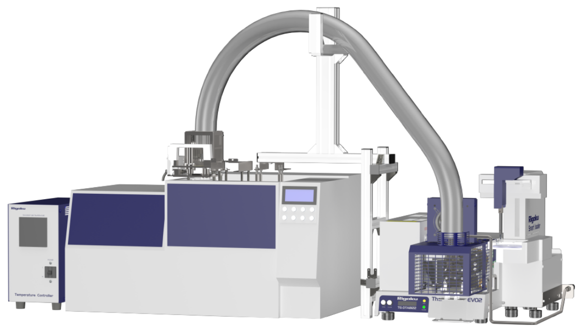

Fig. 6. TG-DTA/GCMS system.

measurements.

3.3 Measurement conditions

Measurements were performed from room temperature (RT) to 1,000°C at 20°C/min under helium atmosphere. The following MS conditions were applied; ionization mode, electron ionization (EI); mass range, m/z 10 to 300; interface temperature, 350°C.

3.4 Results

TG and MS ion thermograms are shown in Figure 8. The mass loss of the Ryugu sample and the Ivuna sample were about 15% and 22%, respectively, from RT to 1,000°C. They demonstrated different profiles of evolved H_2O. In particular, there were significant differences in H_2O evolution between the Ryugu sample and the Ivuna sample in the temperature range below 300°C. The Ivuna sample showed several peaks for H_2O corresponding to a mass loss of about 7%. On the other hand, a minute peak for H_2O was observed in the Ryugu sample corresponding to a mass loss below 1%. There were quite a few differences in H_2O evolution behavior between the Ryugu sample and the CI chondrite at low temperature.

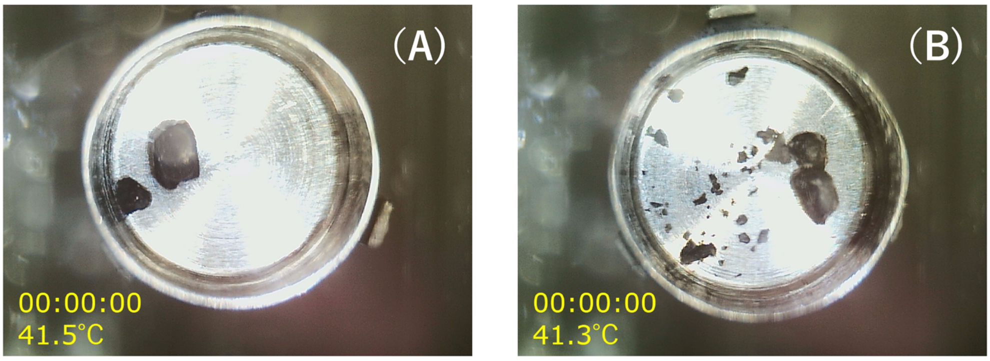

Fig. 7. Sample observation images before measurements.
(A) Ryugu sample, (B) Ivuna meteorite (CI chondrite).
Inner diameter of Pt pan is 4.8 mm.

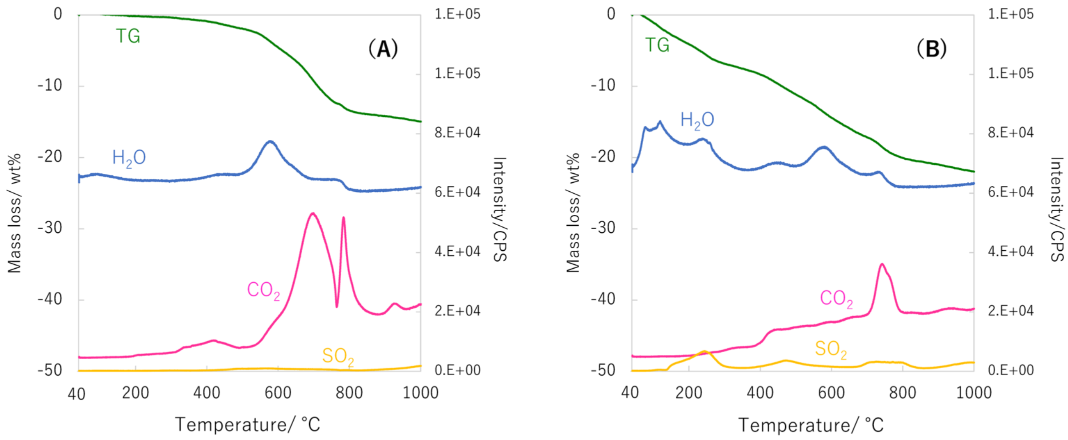

Fig. 8. Thermogravimetric curve and MS ion thermogram.
H_2O: *m*/*z* 18, CO_2: *m*/*z* 44, SO_2: *m*/*z* 64.
(A) Ryugu sample, (B) Ivuna meteorite (CI chondrite).

Table 4. Measurement results of H_2O and CO_2.

Sample	Sample mass (mg)	Mass loss (mass%)	H_2O amount (mass%)	CO_2 amount (mass%)
Ryugu	0.977	15.4	6.8	5.5
Ivuna (CI chondrite)	0.912	22.4	12.7	1.2

Additionally, CO_2 and SO_2 were evolved during heating of the samples.

H_2O and CO_2 were quantified using a calibration curve derived from calcium oxalate monohydrate $CaC_2O_4 \cdot H_2O$, which evolves stoichiometric amounts of H_2O and CO_2 at specific temperatures. Results of quantification are shown in Table 4.

4. Discussion

WDXRF analysis revealed the elemental abundances of the Ryugu sample shows good consistency with the abundances of the CI chondrite meteorite. This indicates the chemical composition of the Ryugu sample is pristine and similar to the solar system abundances. On the other hand, H_2O content by TG-MS is 6.8 mass%, which is more depleted than the 12.7 mass% of the Ivuna meteorite (CI chondrite) and typical water content (20 mass%[4]) of CI chondrite. In a study using a different Ryugu sample (A0219), 7.6 mass% of total H_2O content is reported[8]. These indicate the Ryugu has lower H_2O content than the CI chondrite meteorite. From remote sensing observation by NIR spectrometry, because asteroid Ryugu shows weak absorption at a wavelength of 2.72 μm due to the hydroxyl (OH) band of hydrous minerals, the presence of water in asteroid Ryugu is considered[2]. Since the absorption is weak relative to carbonaceous chondrite, less content of H_2O or less abundance of hydrous minerals is suggested[2]. The depletion of H_2O content of the Ryugu sample compared to CI chondrite is consistent with the observation of asteroid Ryugu.

Low H_2O content in the Ryugu sample can explain the depletion of total oxygen content. When it is assumed that the H_2O content of CI chondrite varies from 20 mass% to 7 mass%, total oxygen content in bulk composition of CI chondrite is calculated as 39 mass% from 46 mass% in representative CI chondrite. This calculated value is in agreement with the analytical result of oxygen content by WDXRF. Therefore, depletion of total oxygen in the Ryugu sample is attributed to low H_2O content.

Unlike the Ivuna meteorite, the Ryugu sample showed a different profile of H_2O evolution at low temperature, consistent with the results by a QEGA (Quantitative Evolved Gas Analysis) study using sample A0219 of Ryugu[8]. In the QEGA study, no H_2O evolution is observed at low temperature[8]. There is a possibility of individual differences among samples or a little bit of moisture absorption by the A0040 sample in this study during transportation from JAXA to the Rigaku laboratory.

5. Summary

Extraterrestrial material recovered from asteroid Ryugu by the Hayabusa2 mission was analyzed by WDXRF and TG-MS. XRF analysis was performed for a small amount of powder sample C0108, which was not pelletized. Twenty-three elements including carbon and oxygen in the Ryugu sample were quantified by the FP method. Elemental abundances determined by XRF were quite consistent with the results of other analytical methods. Determination of total oxygen content demonstrated efficiency in analysis of geological samples containing H_2O. This indicates that it is unnecessary to know accurate H_2O content in samples before XRF analysis.

Elemental abundances of the Ryugu sample show close similarity to the chemical compositions of pristine CI carbonaceous chondrite.

Thermal analysis was performed for a small amount (c.a. 1 mg) of Ryugu sample A0040 and CI chondrite using Thermo plus TG-DTA8122/GC-MS. The Ryugu sample shows lower total H_2O content than CI chondrite. In particular, the TG-MS analysis revealed a significant difference between Ryugu and CI chondrite in the behavior of H_2O evolution below 300°C [1].

XRF and TG-MS analysis have not been conventionally used as analytical techniques for extraterrestrial materials such as meteorites. In this study, XRF and TG-MS played important roles and contributed to scientific results from the Initial Analysis Chemistry Team due to rapid determination of bulk composition. Determination of oxygen and H_2O content was especially important for Ryugu sample characterization because there are not many methods to accurately determine these components in extraterrestrial material.

Acknowledgements

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