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Reductive chemical demagnetization: a new approach to magnetic cleaning and a case study of reef limestones

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Abstract

Chemical demagnetization is not preferred as a demagnetizing method in paleomagnetism because strong acids are cumbersome to handle and require considerable time compared to alternating field and thermal demagnetizations. Particularly, for rocks with carbonate minerals, strong acidic solutions are not applicable. This study presents a new method, termed reductive chemical demagnetization (RCD), using ascorbic acid solution as a reductive etchant. Ascorbic acid is a strong reductive agent and converts Fe^{3+} ions of secondary magnetic minerals to water-soluble Fe^{2+} ions, which facilitate chemical demagnetization of carbonate rocks. The carbonate frame can remain intact if the pH of the solution is buffered at approximately 7 with sodium bicarbonate. This etchant is more suitable than strong acid in terms of handling in a paleomagnetic laboratory, particularly in a magnetic field free room. To reduce the required time, a technique of dripping the etchant on the sample was also devised. This helps the fresh etchant flow through the voids between the grains of rocks to rapidly remove dissolved Fe^{2+} ions. As a case study of RCD, reef limestone samples were examined. The results showed that the dripping experiments with 5% ascorbic acid solution were the most effective. It took 72 h to reach the remaining isothermal remanent magnetization (IRM) constant. Thermal demagnetizations of 3-component IRM indicate that RCD removed the high coercivity remanences carried by hematite and goethite. These magnetic minerals were considered to be precipitated between the grains of the rock, and thus they were dissolved by the RCD treatment. A chemical remanent magnetization (CRM), acquired by secondary magnetic minerals, can easily mask the primary remanence for sedimentary rocks of weak magnetization, and the coercivity or unblocking-temperature spectra of the primary remanence and secondary CRM overlap; however, RCD can effectively remove the secondary CRM. RCD prior to alternating field or thermal demagnetization has the potential to improve paleomagnetic demagnetization of sedimentary rocks.

Keywords: Reductive chemical demagnetization, Reductive etchant, Ascorbic acid, Reef limestone

Introduction

Demagnetization is among the most important techniques in paleomagnetism to extract a primary remanence from natural remanent magnetization (NRM). Alternating field (AF) and thermal demagnetizations are among the most popular techniques, while chemical demagnetization has also been used for sediment paleomagnetism since the 1960s to a lesser extent (e.g., Collinson 1967; Park 1970; Burek 1971).

During the 1960s, detrital remanent magnetization became increasingly important, and the problem of secondarily acquired chemical remanent magnetization (CRM) in sedimentary rocks was widely recognized. In particular, the timing of CRM in red sedimentary rocks was frequently in debate (e.g., Collinson 1967). Kawai (1963) showed demagnetization results of NRM of a volcanic rock using hydrochloric acid (HCl) solution which dissolved magnetite and titanomagnetite in the rock. Collinson (1965) used hydrochloric acid to dissolve pigment hematite in red bed samples

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taken from Triassic Chugwater formation in Wyoming (North America), and discussed the carrier of NRM. Park (1970) conducted acid leaching on red sediments from the Hopewell Group and Cumberland Formation of North America and found the remanences carried by different species of hematite. Two magnetic components were separated by chemical demagnetization using hydrochloric acid solution. They found that the red material removed by the hydrochloric acid solution had secondary CRM. Strong acids (e.g., hydrochloric acid) have been mostly used as etchants for chemical demagnetization, which is also known as "chemical leaching" (Park 1970; Collinson 1967; Channell et al. 1993). This type of chemical demagnetization has three drawbacks: (1) it uses strong acids that require careful handling in draft chamber. However, draft chamber system, yielding magnetic noises, is very difficult to be set in a magnetically shielded room. (2) it is time-consuming (approximately 1 month) and some samples need treatment at high temperatures (100 °C: Henry 1979); and (3) it cannot be applied to calcareous sediments or sediments that contain considerable amounts of carbonate grains because strong acid dissolves the main grains of the sediments (e.g., Tauxe et al. 1980). Thus, chemical demagnetization has rarely been used in paleomagnetic studies.

Other than strong acid for leaching magnetic minerals, Mehra and Jackson (1958) used a dithionite-citrate system buffered by sodium bicarbonate ($NaHCO_3$) for refining X-ray diffraction patterns of magnetic minerals. Kirschvink (1981) suggested the use of the same system for chemical demagnetization. Bonhommet et al. (1981) attempted chemical leaching using an oxidant solution of sodium sulfite (Na_2SO_3) for the Alba formation in Northwest Spain, although the experiments were not successful.

The advantage of chemical demagnetization is that the etchant first reaches the magnetic minerals precipitated at the surface of the sedimentary grains, which can carry secondary magnetizations (e.g., secondary CRM). Tauxe et al. (1980) applied chemical demagnetization to Miocene red bed samples, collected from the Siwarik group in the Khaur area in northern Pakistan, for rock magnetic analysis, which contributes to the interpretation of the result of conglomerate test to identify the primary component. Thus, chemical demagnetization can be useful as these types of sediment are widely distributed.

In this study, we present a new type of chemical demagnetization using a reductive etchant instead of strong acids. As a case study of this chemical demagnetization method, we investigated reef limestone samples from Ryukyu group in Japan (Anai et al. 2017). Etchant supply methods and efficient concentration of the etchant for effective chemical demagnetization on remanent magnetization are discussed in this paper.

Study site and previous investigation

The study site is the Ryukyu Group on Miyakojima Island, Okinawa, Japan. The paleomagnetism of the limestones of the Ryukyu Group has been published by Anai et al. (2017). The results of this previous investigation are summarized below.

The Ryukyu Group on Miyakojima Island was divided into five units by sequence-stratigraphy (Yamada and Matsuda 2001), and the age of these units was assigned by calcareous nannofossil datum (987–451 ka). Paleomagnetic samples were collected at 20 sites from all five units (MY-Unit 1–5 from oldest to youngest). For specimens from most of the 20 sites, AF demagnetization and thermal demagnetization were applied. Moreover, reductive chemical demagnetization (RCD) and subsequent AF demagnetization were applied to specimens from 18 sites. The AF demagnetization did not separate a characteristic remanent magnetization (ChRM). Thermal demagnetization provided more reliable data than AF demagnetization from some sites, but the most effective demagnetization method was a hybrid treatment consisting of RCD and subsequent AF demagnetization. Secondary remanences were effectively removed by the RCD and AF demagnetization, and ChRM directions were recognized for 13 of the 18 sites. Thus, all specimens were demagnetized by thermal demagnetization and RCD + AF demagnetization.

Table 1 shows the paleomagnetic direction data from Anai et al. (2017). These directions were selected using the criterion of maximum angular deviation (MAD) $\leq 15°$. The virtual geomagnetic pole (VGP) latitudes for all specimens are plotted as shown in Fig. 3. The polarity transition found in the lowest part of the MY-Unit 4 is identified as the Matuyama–Brunhes boundary. Noteworthy sites are Q-43-2 (MY-Unit 4) and Q-28, Q-4 (MY-Unit 1). These sites showed normal polarity with thermal demagnetization, but, Q-28 and Q-4 gave a reversed polarity with RCD + AF demagnetization. In contrast, Q-43-2 showed the same polarity with both demagnetization methods. Anai et al. (2017) also performed RCD + thermal demagnetization for these sites and obtained the same polarity as the RCD + AF demagnetization. These results suggest that the Ryukyu limestone acquired a secondary magnetization that cannot be demagnetized by thermal or AF treatments alone. The better concentration of ChRM directions and clear polarity change indicate that RCD is very effective.

Table 1 Paleomagnetic results from the Ryukyu Group in the Miyakojima Island (Anai et al. 2017)

Unit	Site	Latitude (N)	Longitude (E)	Elevation (m)		Facies	NRM (mA/m)	N_0 (all samples)			N (MAD < 15°)			D (°)	I (°)	α95 (°)	k	VGP	
				Area A	Area B		avarage	TD	RCD + AFD	Total	TD	RCD + AFD	Total					Latitude	Longitude
1	Q-4	24°42′35″	125°18′54″		3.0	R	1.10	6	4	10	1*	2	2	(132.6)	(− 31.0)	(10.7)	(550.4)	− 45.1	215.6
1	Q-28	24°44′42″	125°15′38″	4.5		R	0.725	8	5	13	1*	2	2	(186.7)	(− 40.3)	(60.3)	(19.4)	− 83.7	25.2
2	M-12	24°46′00″	125°17′03″	18.5		C	0.224	6	6	12	0	2	2	(196.6)	(− 34.2)	(18.3)	(188.4)	− 73.5	21.1
2	P-35	24°42′43″	125°19′08″		18.0	C	14.0	7	6	13	0	3	3	194.8	− 33.7	21.6	33.6	− 74.9	18.2
2	A-10	24°42′59″	125°18′38″		21.3	C	1.06	6	5	11	0	2	2	(144.5)	(− 29.7)	(57.2)	(2.5)	− 55.7	221.4
2	N-10	24°45′00″	125°17′30″	21.0		C	0.0765	7	5	12	0	2	2	(218.0)	(− 35.3)	(18.0)	(47.9)	− 54.5	34.9
2	P-16	24°43′09″	125°18′48″		24.5	C	0.306	7	7	14	0	3	3	187.0	− 32.1	31.8	16.0	− 80.4	1.2
3	P-23	24°43′13″	125°19′00″		27.5	R	0.0754	7	6	13	1	2	3	199.4	− 33.1	21.3	330.8	− 70.9	22.2
3	Q-43	24°44′11″	125°20′50″		31.0	R	0.867	7	5	12	0	2	2	(175.2)	(− 22.6)	(14.1)	(317.6)	− 76.5	93.9
3	Q-31	24°43′09″	125°20′30″		32.0	R	10.7	6	7	13	0	4	4	190.3	− 34.9	23.1	16.8	− 79.1	13.5
3	N-8	24°43′15″	125°17′54″	30.0		R	0.0752	6	6	12	2**	1	2	(178.5)	(− 33.8)	(52.8)	(24.5)	− 83.9	91.1
4	P-18	24°43′20″	125°18′55″		34.5	R	1.44	5	6	11	0	3	3	194.7	− 45.3	26.0	23.6	− 76.5	46.2
4	Q-31-2	24°43′20″	125°20′30″		36.5	R	0.368	7	5	12	2	0	2	(347.9)	(38.4)	(12.6)	(96.8)	78.0	25.5
4	Q-43-2	24°43′13″	125°20′50″		37.0	R	1.57	7	6	13	2	1	3	21.2	38.9	23.6	113.8	70.3	217.8
4	Dd-5	24°44′33″	125°18′02″		51.0	R	0.0976	6	2	8	4	0	4	358.7	47.6	4.6	399.9	85.6	88.4
4	Ee-10	24°44′13″	125°21′40″		70.5	R	0.954	6	2	8	3	0	3	354.7	35.5	11.6	114.6	83.1	0.4
5	Aa-18	24°47′21″	125°18′30″	49.5		C	2.35	5	3	8	2	1	3	351.1	37.4	21.8	32.9	81.0	17.4
5	Cc-17	24°45′37″	125°19′05″	54.0		C	0.235	6	0	6	4	0	4	354.8	33.2	5.2	168.2	82.0	354.7
5	Cc-13	24°45′47″	125°19′14″	63.0		C	0.873	6	2	8	3	0	3	9.0	36.0	35.8	12.9	80.5	236.9
5	Cc-14	24°45′46″	125°19′14″	65.0		C	0.463	6	0	6	5	0	5	347.0	31.9	20.9	14.3	75.9	12.2

N_0: number of specimens used to measurement paleomagnetic direction, the row of N_0; TD: number of specimens treated with thermal demagnetization (TD), RCD + AFD: number of specimens treated with combination procedure reductive chemical demagnetization (RCD) and Alternating field demagnetization (AFD). N: number of specimens with MAD < 15°. D and I: declination and inclination of site mean direction, which is calculated from the specimens passed the criteria, respectively. α_{95}: 95% confidence limit; k: precision parameter; facies of R and C: rhodolith limestone and coral-bioclastic-limestone, respectively. Parenthesis are reference value ($n \leq 2$). *: these samples were not used to calculate a site mean palaeomagnetic direction. **: one sample was not used to calculate a site mean palaeomagnetic direction. These samples gave inconsistent directions

Methods

RCD is a method that uses a reductive etchant instead of a strong acid. It is based on the characteristics of the iron ions: ferrous iron (Fe^{2+}) is water soluble, while ferric iron (Fe^{3+}) is not (Kirschvink 1981). Secondary magnetic minerals that form in oxic conditions, such as goethite or pigment hematite, which precipitate in voids between particles of samples, are composed of Fe^{3+}. When such magnetic minerals are exposed to reductive agents, ferric iron is reduced to ferrous iron and thus the minerals are dissolved into the solution.

A new method of chemical demagnetization

In this study, we devise two points of improvement and propose a new method of chemical demagnetization. First, a strong reducing agent is applied as an etchant instead of a strong acid. The strength of reductant agent is often represented by pE, the oxidation/reduction potential. The lower the pE, the stronger the reductant. An oxidizing species is stable at a low pE, namely ferrous iron is more stable than ferric iron. The etchant is required to have a low pE and a near-neutral pH. Figure 1 shows the pE versus pH equilibrium diagram of the Fe-S-H_2O system as modified from Garrels and Christ (1965) and Henshaw and Merrill (1980). The diagram contains magnetic minerals which could be included in sedimentary rocks, although the samples in this study contain no iron sulfides.

We selected two strong reductants: ascorbic acid ($C_6H_8O_6$) and potassium iodide (KI). These reductants are listed as the strongest organic and inorganic reductive agents with ease of handling (Moeller 1952; Fieser and Fieser 1961). Dithionite has often been used in sediment studies to dissolve ferric minerals (e.g., Mehra and Jackson 1958; Kirschvink 1981). However, for paleomagnetic studies, we need to treat large number of specimens (volume: ~ 10 cc) in the magnetic free space, while the dithionite treatment requires a draft chamber system. In contrast, ascorbic acid solution is applicable to many paleomagnetic samples simultaneously in the magnetically shielded room without a draft chamber. The ascorbic acid solution is also safe to be handled by paleomagnetists with little experience in experimental chemistry and can be disposed of with ease. Afonso et al. (1990) showed that magnetite and hematite were dissolved by ascorbic acid solution under controlled conditions of concentration and temperature. They showed that hematite was dissolved at 25 °C while magnetite needed higher temperatures for dissolution. They also indicated a solution with a higher concentration dissolves magnetite and hematite faster. The pH of the ascorbic acid solution is approximately 2.5, a value at which carbonate rocks dissolve. Therefore, we adjusted the pH to a near-neutral value using sodium bicarbonate ($NaHCO_3$) as a buffer material. The adjusted ascorbic acid solutions had the values indicated by the circles shown in Fig. 1 (the pE is from −1.69 to −0.85 and the pH is from 5.5 to 6.5). Potassium iodide is among the most popular reductive agents in inorganic chemistry. The iodide ion (I^-) is widely recognized to have a strong reductive reaction and antioxidative effect. The pH of KI solution is approximately 7 and it has the value indicated by the square in Fig. 1 (the pE is approximately −2.0 and the pH is approximately 7.0).

Second, a dripping supply of the etchant (Fig. 2) was developed and used in this study. The flow velocity of the etchant was controlled by a medical drip infusion set (Terufusion Infusion set, TI-J352P, TERUMO Co. Ltd.) which provided good control of the solution rate. Sedimentary rocks commonly acquire CRM via the precipitation of magnetic minerals associated with water passing through constituent grains, mainly when the outcrop is exposed or shortly after deposition. In the etchant flow system, the etchant continuously flows between the sedimentary grains of the specimen, efficiently reducing ferric ions to ferrous ions and more rapidly carrying ferrous ions out than in a state without flow such as the dipping method where a specimen is immersed in a solution in a beaker, as advection

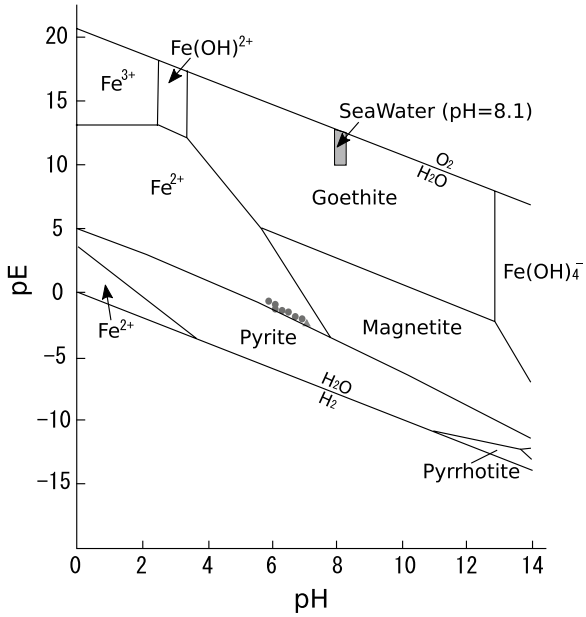

Fig. 1 pH versus pE equilibrium diagram of the Fe–S–H_2O system, modified from Garrels and Christ (1965) and Henshaw and Merrill (1980). The pH and pE of the reductive etchant should be adjusted to plot in the Fe^{2+} area. Circle symbols indicate the etchant comprising the ascorbic acid solution buffered with sodium bicarbonate. Triangle symbol indicate the KI solution

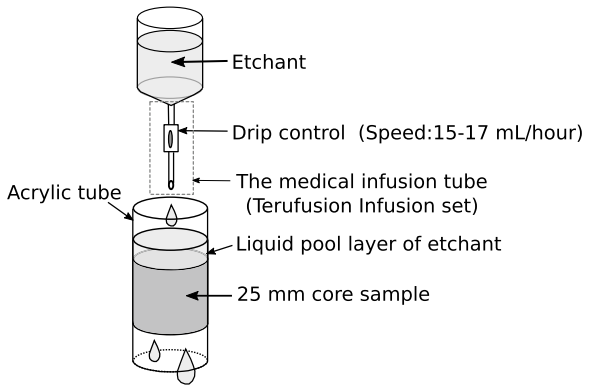

Fig. 2 Schematic diagram of the new chemical demagnetization method with the dripping apparatus. A medical infusion tube is affixed to control the dripping rate

is more rapid than diffusion. As the etchant directly reaches the precipitated secondary magnetic minerals in the voids between the particles of the samples, RCD, as well as chemical leaching, are expected to be efficient at removing secondary magnetic minerals related to these CRM.

Samples

The samples used in the present study are the same as those used by Anai et al. (2017). The samples are reef limestones composed of particles of various sizes including coral fossils with bioclastic structures. The grain sizes of matrix were approximately 0.03–0.06 mm and fossils included in the reef limestones had the dimension of approximately 0.1–10 mm. The facies of the samples were coral-bioclastic limestone and rhodolith limestone. The samples were generally white, but their voids were reddish-brown to yellowish-brown in color (Fig. 5a). The permeability of the samples was approximately 1×10^{-9} m^2. We prepared the sister specimens from a core for each comparison experiment. They were visually similar in color and porosity, and thus likely had a similar degree of diagenesis. The sample names are composed of the site name (see Fig. 3), core number, and specimen number.

Chemical demagnetization experiments

Effects of ascorbic acid dripping and dipping

Five drill core samples were prepared, which were collected from five sites: two of the five sites were in coral limestone (sites N-10 and Cc-13) and three other sites were in rhodolith limestone (sites Q-4, N-8, and Q-31-2). Four sister specimens were cut from each of the five core samples. The four sister specimens were used for the dripping or dipping experiments with ascorbic acid or KI etchants. All experiments were performed at room temperature. Isothermal remanent magnetization (IRM) was imparted to two of the sister specimens in a field of 3 T, parallel to the Z-axis of the specimens, using an impulse magnetizer, ASC Model IM10-30 (ASC Scientific). IRM measurements were made using a fluxgate-sensor spinner magnetometer,SMM-85 (Natsuhara Giken), at Kumamoto University.

The etchant used was 5% ascorbic acid solution, with an adjusted pH of 6.5 with sodium bicarbonate and 5% KI solution (pH = 7.0). An apparatus was designed for the dripping experiments (Fig. 2), and the solution dripping rate was adjusted such that the etchant pooled 10 mm in thickness above the upper surface of the specimen. The dripping rate was 15–17 ml/h. The IRM was measured every 12 h. The large decrease in IRM stopped at 72–96 h in all experiments, and thus, the measurements were made up to 120 h.

A sister specimen was subjected to chemical demagnetization using a conventional dipping procedure: the specimen was simply immersed in the reductive etchant in a beaker. The solution was adjusted to the same condition as the dripping experiment. The amount of etchant in the beaker was 350 ml to immerse the entire specimen. The IRM was measured every 12 h.

The samples were observed under an optical microscope to compare the change in color by the dripping RCD treatment. Electron microscopy and energy-dispersive X-ray spectroscopy (EDS) analyses were conducted on the untreated sample with a HITACHI Miniscope TM3030Plus.

Ascorbic acid dripping with different concentrations

To draw a comparison between the variations in response to the concentration of etchant, IRM-acquired samples were subjected to ascorbic acid dripping at different concentrations (5, 10, 15, and 20%) and IRM was measured every 24 h. IRM was imparted to the Z-axis of the specimens. Two core samples were prepared, which were collected from a site of coral limestone (site A-10) and another site of rhodolith limestone (site N-8). Four sister specimens were cut from each of the two core samples.

Rock magnetic properties before/after RCD

Rock magnetic experiments were conducted to investigate the relation between the effect of RCD and the contained magnetic minerals. Twelve core samples were collected from 12 sites; 5 sites were coral-bioclastic limestone (sites M-12, A-10, P-16, Aa-18, and Cc-14) and 7 sites were rhodolith limestone (sites Q-28, Q-43, Q-31, N-8, P-18, Q-43-2, and Dd-5). Two sister specimens were

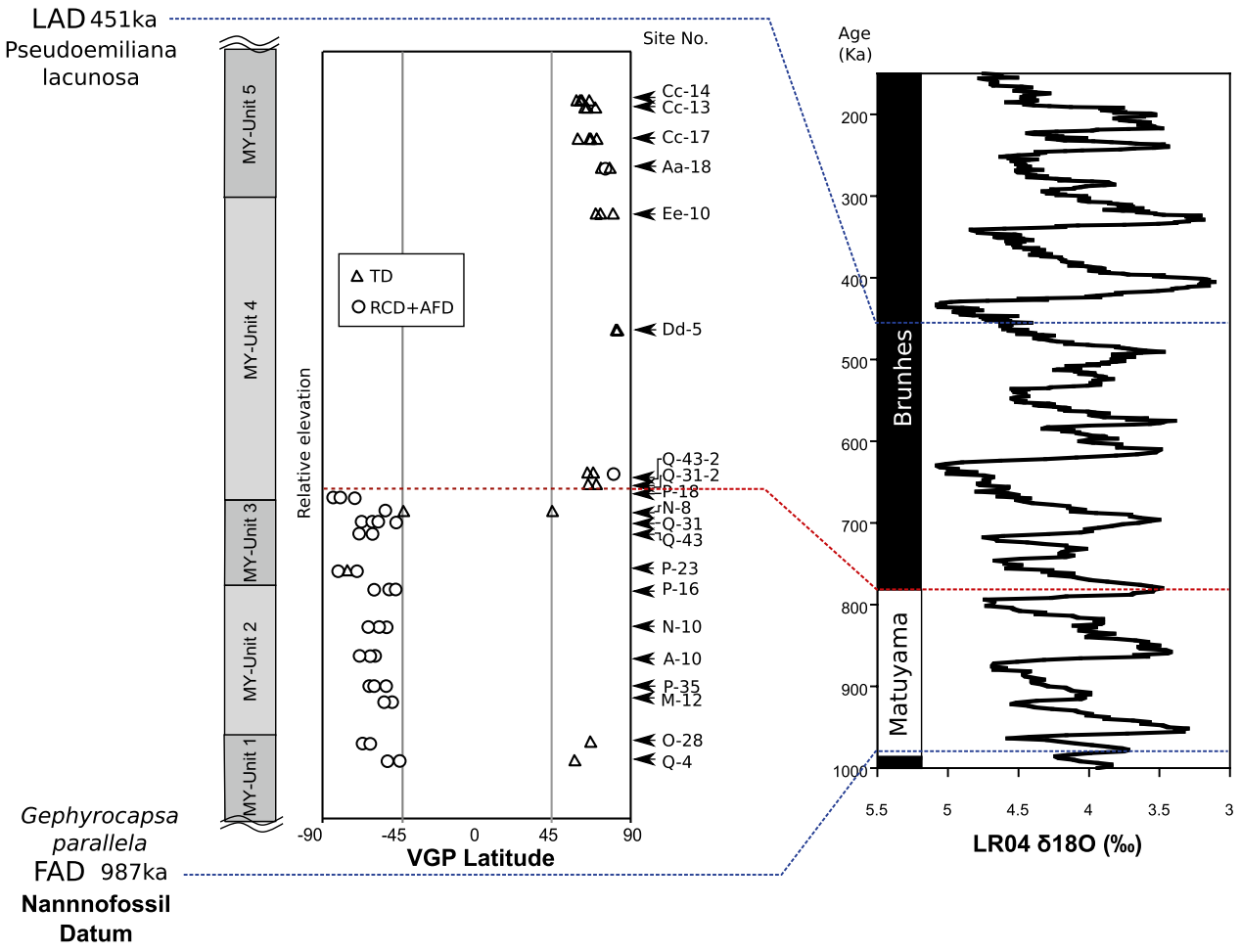

Fig. 3 Magnetostratigraphy of the Ryukyu Group on Miyakojima Island, Okinawa, Japan (modified from Anai et al. 2017). The Virtual Geomagnetic Pole (VGP) latitude for each specimen is plotted along the stratigraphic column. The samples used in the present study were taken from these sites. The geochronological constraints were provided by the magnetostratigraphy and biostratigraphy

cut from each of the 12 core samples. One of the sister specimens was subjected to RCD with ascorbic acid solution dripping, and the other was without RCD, for all 12 cores. The IRM acquisition experiment was first applied to these specimens. The IRM was imparted parallel to the Z-axis (cylinder axis) of the specimens in progressive steps up to 3.0 T and the strength of remanence was measured at each step.

After the IRM acquisition experiment, three directional IRM components were imparted to the specimens, which were not demagnetized between experiments. For the directional IRM acquisitions, a magnetic field of 3.0 T was applied to the Z-axis of the specimens, and subsequently, a field of 1.0 T was provided to the Y-axis. Finally, a field of 0.3 T was applied to the X-axis. The IRM-acquired samples were thermal demagnetized with a TDS-1 (Natsuhara Giken) in steps of 25–50 °C up to 700 °C.

Results

Results of ascorbic acid dripping and dipping

Experimental results of RCD using an etchant of ascorbic acid or KI solution by the "dripping method" and "dipping method" are compared as shown in Fig. 4.

In the dripping method of ascorbic acid solution, approximately 75% of the initial IRM of the sample remains at 24 h. Thereafter, 65% of the initial IRM remains until 72 h. There is no clear decrease during 72–120 h. The overall demagnetization is 35% of the initial IRM. The dipping method of ascorbic acid solution showed approximately 85% of the initial IRM remains at 12 h. It continued to decrease and 74.5% remains at 120 h.

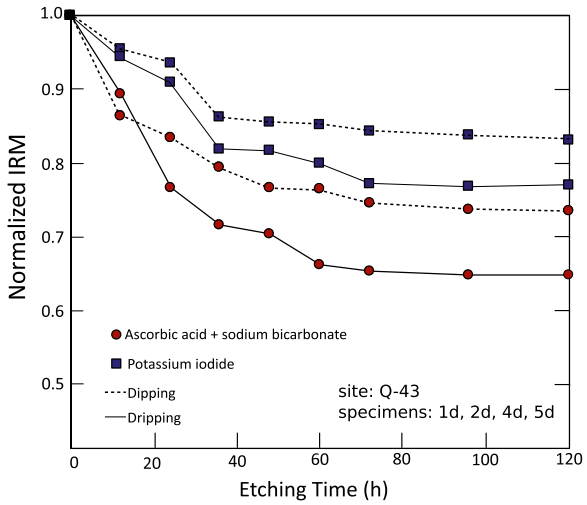

Fig. 4 Isothermal remanent magnetization (IRM) variation during the chemical demagnetization using reductive etchants. Circles (squares) indicate the results of ascorbic acid solution (potassium iodide solution). Solid and dashed lines denote the results of the dripping and dipping methods, respectively. Ascorbic acid + dipping is specimen 1d, ascorbic acid + dripping is 2d, potassium iodide + dipping is 4d and potassium iodide + dripping is 5d, respectively

Compared to the experiments using ascorbic acid solution, experiments using KI solution have a low demagnetization rate using both the dripping and dipping methods. In the dripping method, 75% of the initial IRM remains at 72 h. In the case of the dipping method, only approximately 82% of the initial IRM remains at 120 h.

From these experimental results, we can recognize the chemical demagnetization time required for both the dripping and dipping methods. As shown in Fig. 4, in the dripping experiments, the demagnetization curves are nearly constant after 72 h. Therefore, we concluded that the time required for the reef limestone using the dripping method was 72 h. In the dipping method, the clear decrease in IRM finished until 72 h, but the IRM continued to slightly decrease even after 72 h.

Under the optical microscope, reddish-brown to yellowish-brown deposits are found in the voids of the untreated sample as shown in Fig. 5a. In contrast, the matrix is white to off-white. In the sample following the RCD using ascorbic acid dripping (Fig. 5b), reddish-brown adherents were substantially removed in both intergranular and void surfaces. In the sample treated with the RCD of KI solution (Fig. 5c), the intergranular color changed to a light yellowish-brown color. The difference in sample weight before and after RCD is about 0.1% or smaller. The results of EDS analysis on the untreated sample (Fig. 5d–g) show that Fe is distributed in the voids.

Results of ascorbic acid dripping with different concentrations

The RCD results of different ascorbic acid concentrations are shown in Fig. 6. As a result, 5% ascorbic acid solution was found to be suitable for chemical demagnetization using a reductive etchant (Fig. 6). The 5% solution demagnetized magnetization by approximately 30% of the initial IRM at 72 h. The other solutions (10%, 15%, and 20%) demagnetized magnetization by approximately 10–15% of the initial IRM. As a reductive etchant using ascorbic acid in the dripping procedure, an ascorbic acid concentration of 5% was sufficient to effectively demagnetize the samples used in this study.

From the results of these experiments and observations, it was concluded that the effective method of RCD was dripping of 5% ascorbic acid solution.

Results of rock magnetic experiments

Results of the IRM acquisition experiment

Figure 7 shows the IRM acquisition curves for the specimens with and without the RCD treatment. Figure 7a shows the results for sister specimens of a core sample taken from site A-10, which is in coral-bioclastic limestone. Figure 7b shows the results from site N-8, which is in rhodolith limestone. Because 12 experiments showed similar results, representative examples of coral-bioclastic limestone and rhodolith limestone are shown. The IRM did not saturate in fields up to 3.0 T for the specimens without RCD (blue circles in Fig. 7). This suggests that the samples contain magnetic minerals with high coercivity. However, the IRM saturated at approximately 0.2 T for the samples subjected to RCD (red triangles in Fig. 7). It can be inferred that the magnetic grains removed by RCD have a coercivity between 0.3 and 3 T.

Results of thermal demagnetization of 3-component IRMs

Figure 8a, c shows the results without the RCD treatment, and Fig. 8b, d shows the results with the RCD treatment before the thermal demagnetization of 3-component IRMs. The results shown in Fig. 8 are obtained from the specimens which were subjected to the IRM acquisition experiment (Fig. 7). As shown in Fig. 8a, c, a rapid decrease of 100–150 °C occurs in the low ($\leq$0.3 T) and middle coercivity (0.3–1 T) components. The low coercivity component is mostly demagnetized at approximately 600 °C. The middle coercivity component (0.3–1 T) and high coercivity component (1–3 T) are completely demagnetized at 675 °C, which suggests the presence of hematite. As shown in Fig. 8b, d, the high and middle coercivity components are nearly zero after the RCD treatment indicating that the RCD treatment removed the magnetic minerals of the high and middle coercivity components from the samples.

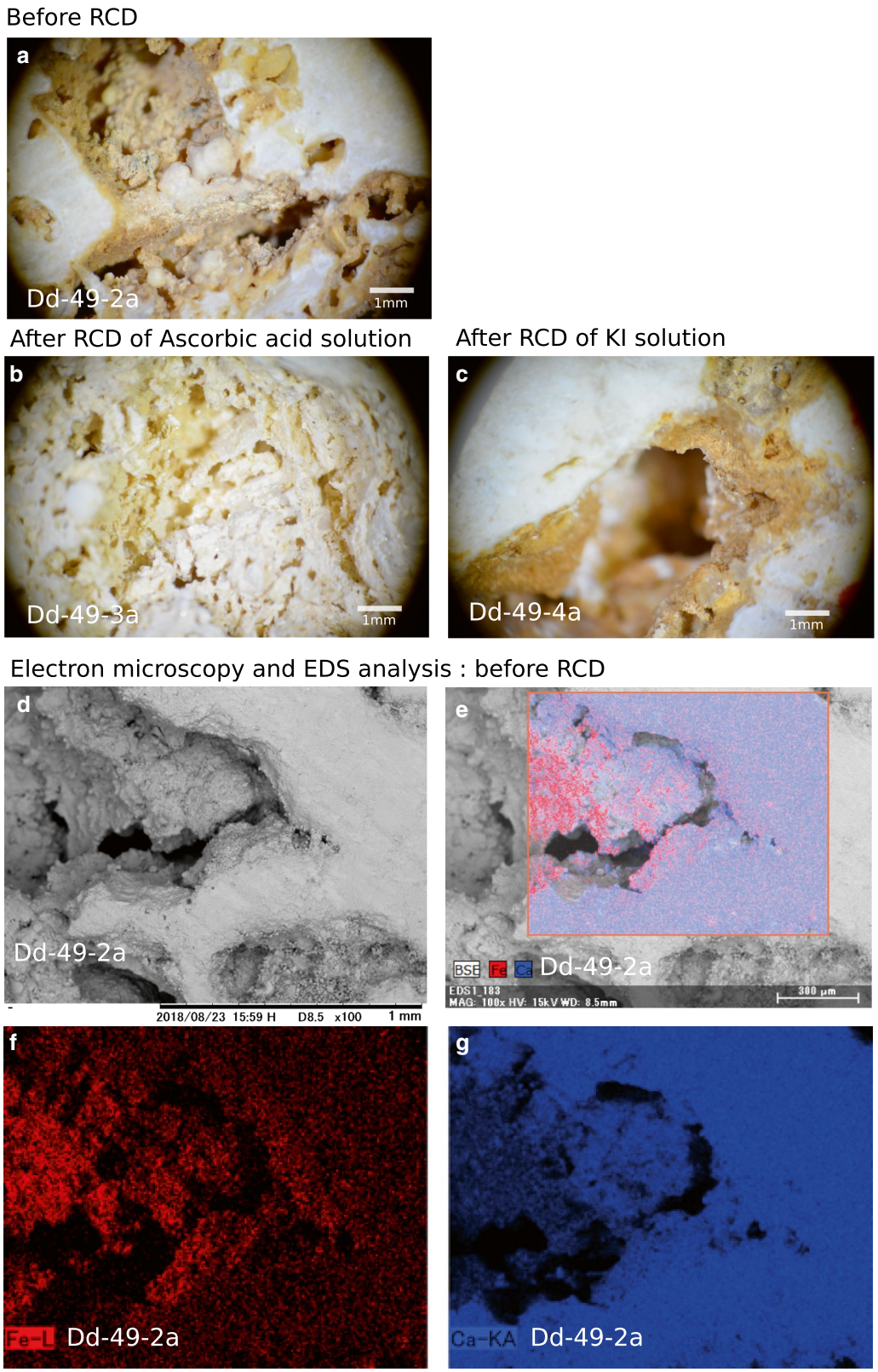

Fig. 5 Photograph of the surface of the specimens before and after the reductive chemical demagnetization (RCD) and electron microscopic observation on specimen before RCD. **a** Specimen before RCD. **b** Specimen after RCD of ascorbic acid solution. **c** Specimen after RCD of potassium iodide solution. **d** Specimen before RCD (the same specimen as (**a**)). **e** The area of EDS analysis. **f** Distribution of Fe. **g** Distribution of Ca

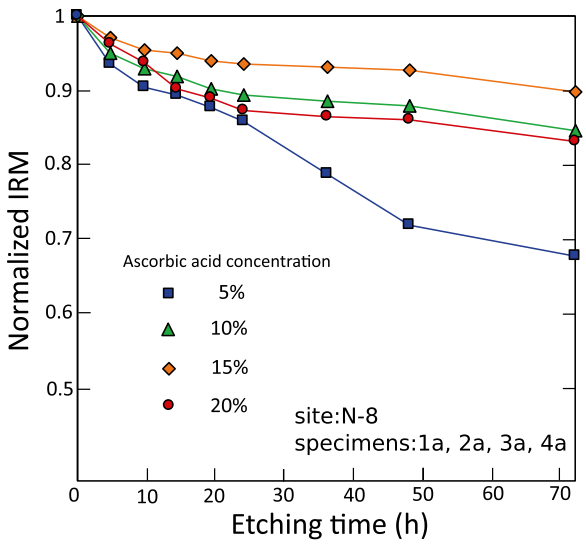

Fig. 6 IRM variation during RCD with ascorbic acid of different concentrations. The experiments were confirmed in 72 h using the dripping method. The experiments were applied for 2 core sample which was cut 4 sister specimens. The 2 sites were coral-bioclastic limestone and rhodolith limestone, respectively. The square, triangle, rhombus, and circle symbols are 5% (specimen: 4a), 10% (specimen: 3a), 15% (specimen: 2a) and 20% (specimen: 1a) ascorbic acid solution concentration, respectively

Based on the results of the IRM acquisition curve (Fig. 7) and thermal demagnetization of the 3-component IRMs (Fig. 8), the magnetic minerals contained in the samples were estimated. Table 2 shows the spontaneous magnetization, coercivity ranges, and ordering temperatures for typical magnetic minerals. As shown in Fig. 8a, c, the low coercivity component rapidly decays at 150 °C and 580 °C. The magnetic minerals responsible for this are goethite and magnetite, respectively. This is corroborated by the observed coercivity range. The middle coercivity component decays at 150 °C and 675 °C. The magnetic minerals responsible for this are goethite and hematite, respectively. The magnetic minerals contained in the samples (without RCD) are thus goethite, magnetite, and hematite. The samples with the RCD treatment show that the high and middle coercivity components are clearly demagnetized (Fig. 8b, d).

Discussion

Chemical demagnetization has been conventionally conducted by dipping samples in a strong acid (e.g., Park 1970). However, as strong acids are cumbersome to handle and cannot be applied to carbonate rocks, chemical demagnetization has not been extensively used in paleomagnetic studies. This research attempted to devise a rapid and versatile chemical demagnetization method.

From the results of several experiments, a new method of chemical demagnetization, RCD, was developed. The RCD used a reductive etchant comprising ascorbic acid (5%) buffered with sodium bicarbonate. The etchant of strong reductants converts the Fe^{3+} into water-soluble Fe^{2+} and has a near-neutral pH, thus RCD has potential applicability to rocks. However, for application to other materials, it is necessary to conduct fundamental experiments on the concentration of etchant and demagnetization time, and magnetic measurements to assess the effect of RCD.

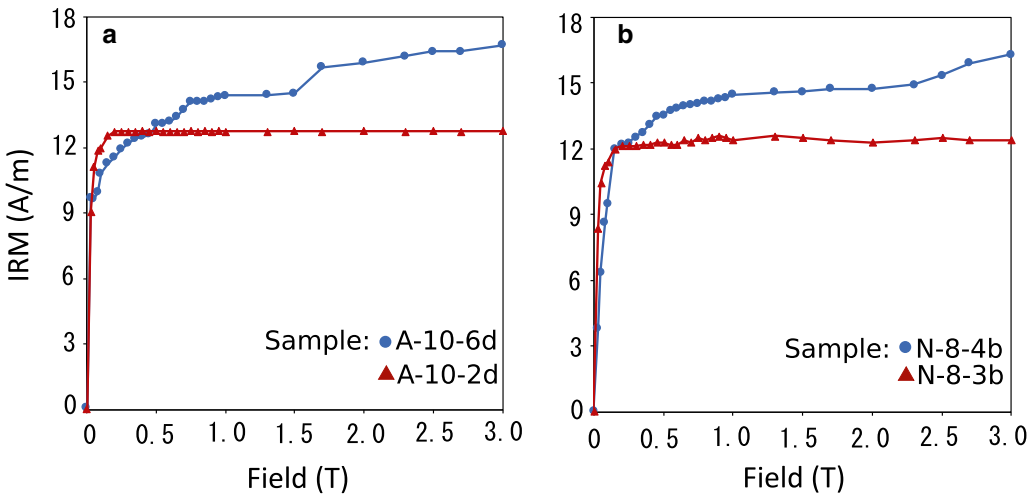

Fig. 7 IRM acquisition curves of specimens with and without RCD. Circle symbols denote the results without RCD. Triangle symbols show the results with RCD. **a** Shows the results of a sister specimen of a core sample taken from site A-10, which is in coral-bioclastic limestone. **b** shows those from site N-8, which is in rhodolith limestone

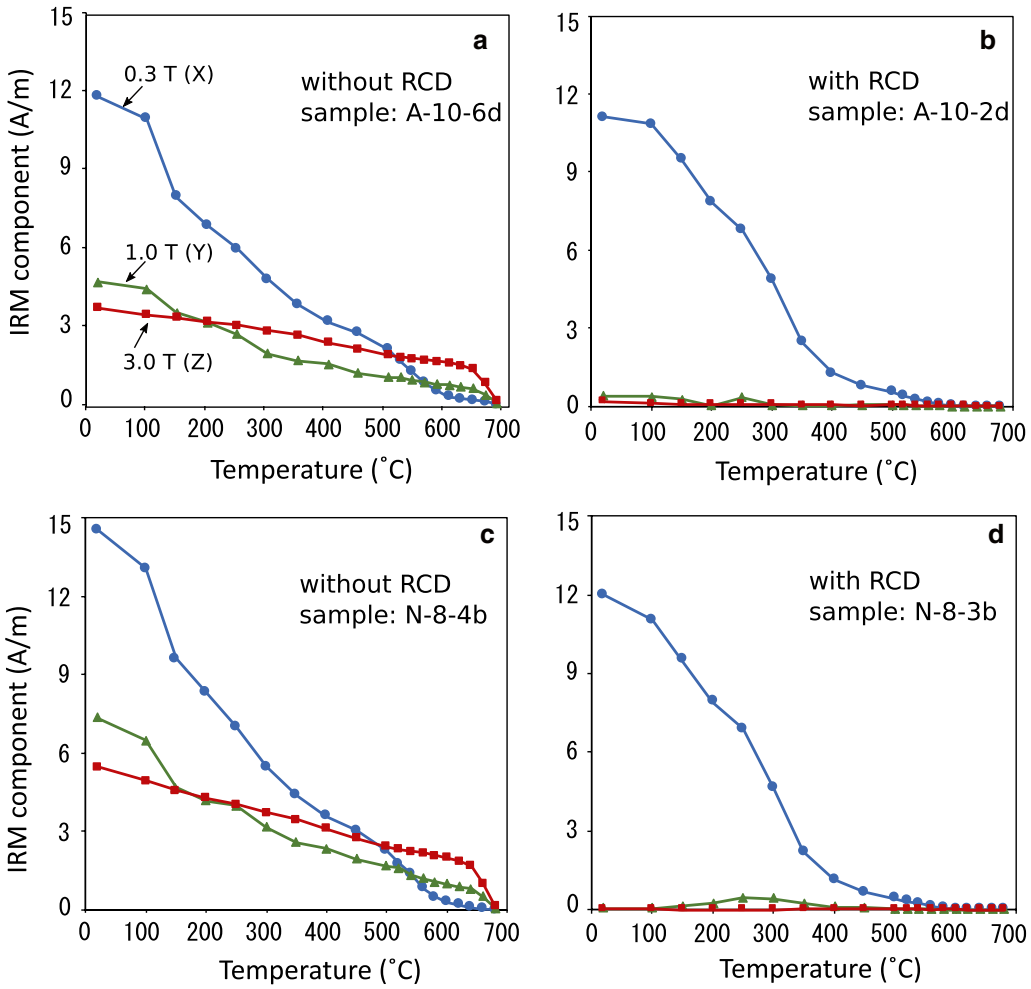

Fig. 8 Results of progressive thermal demagnetization of the 3-component IRMs. **a**, **c** Show the results without RCD, **b**, **d** show those with RCD. Applied fields are 3.0 T for the *Z*-axis of the specimens, 1.0 T for the *Y*-axis, and 0.3 T for the *X*-axis

The 5% solution is more effective than 10–20% solutions in our experiments. The reason why the 5% solution is most effective is unclear. Chemical reactions between mineral particles in the reef limestone samples and solutions may be complex, and detailed experiments are required to elucidate this issue.

The magnetic minerals removed by RCD were investigated using the temperature and coercivity spectra observed in the IRM experiments. The magnetic minerals contained in the Ryukyu limestone are magnetite, hematite, and goethite (Fig. 8a, c). This is consistent with the IRM acquisition curves without RCD that does not saturate at 0.3 T (Fig. 7), because hematite and goethite have coercivities larger than 0.3 T (Table 2). The results of progressive thermal demagnetization of the 3-component IRMs after RCD suggest that the magnetic mineral contained in the matrix of the samples is magnetite. The IRM acquisition curves with RCD support this interpretation; the high- and middle coercivity components (1–3 T and 0.3–1 T) were effectively removed by RCD (Fig. 8b, d). As noted above, the optical microscopic observation indicated that the reddish-brown to yellowish-brown deposits precipitated in the voids, likely hematite and goethite, were removed by the RCD treatment. In addition, the results of electron microscopy showed that Fe was observed in the voids of the untreated samples. Thus, the deposits probably include secondary hematite and/or goethite. Moreover, fine-grained magnetite that secondarily crystalized between voids of samples might be removed by RCD. The primary magnetite grains are probably contained

Table 2 Rock magnetic properties of magnetic minerals

Magnetic mineral	Composition	Range of coercivity	Ordering temperature (°C)
Magnetite	Fe_3O_4	10–100 mT	580
Hematite	α-Fe_2O_3	100s of mT to several T	675
Goethite	α-FeOOH	5–10 T	120

References: Dunlop and Özdemir (1997) and Kodama and Hinnov (2015)

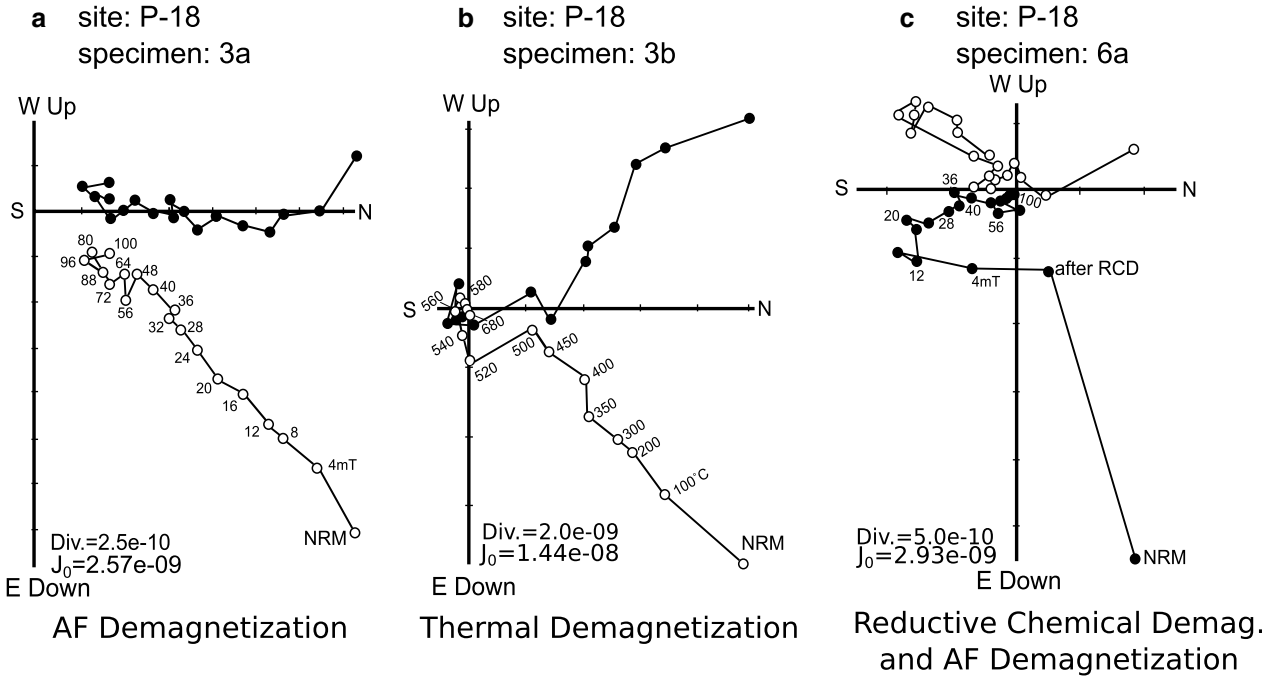

Fig. 9 Typical examples of orthogonal vector plots of stepwise demagnetization on the NRM of the reef limestone samples. **a** Result with AF demagnetization. NRM remains after 100 mT. **b** Thermal demagnetization removes NRM more efficiently than AF demagnetization, but the characteristic ChRM direction is not always identified. **c** The sample was subjected to RCD before AF demagnetization. A relatively large secondary component of NRM was demagnetized via RCD, and NRM was completely demagnetized via AF demagnetization. The specimens labeled **a**, **c** were sister specimens, and **b** was taken from adjoining core in a same site (P-18)

in the matrix part of the samples, and thus they are not affected by the ascorbic acid solution.

The study is also consistent with the result that AF demagnetization up to 100 mT without the RCD treatment does not completely demagnetize the NRM (Fig. 9a).

The new dripping method was tested for RCD. The etchant continuously flowed through the voids between the particles of the specimens. Rock magnetic experiments suggest that the magnetic minerals removed by the RCD treatment were hematite and goethite.

We propose that RCD can be used to improve paleomagnetic studies in sedimentary rocks. A major issue in paleomagnetic studies is that samples sometimes have a very weak NRM. A CRM, acquired by secondary magnetic minerals, can easily mask a small primary remanence, and the coercivity or unblocking-temperature spectra overlap (Fig. 9b). Such a case was brought forward by Sakai and Jige (2006) and Anai et al. (2017) who reported on the magnetostratigraphy of reef limestone in the Ryukyu Group. These studies found cumbersome secondary components in the reef limestones. The challenges in magnetic measurement of reef limestones are twofold: (1) the samples have very weak NRM and (2) conventional demagnetization techniques, AF and thermal demagnetizations, often do not separate the primary component from the NRM because the secondary components mask the primary component (Fig. 8a, b). Anai et al. (2017) investigated the magnetostratigraphy of reef limestones used in the present study and determined that a secondary CRM was present in the limestone, and RCD was effective at

removing the carrier minerals of that CRM. They determined that the high coercivity magnetic minerals carrying secondary components were hematite and goethite via rock magnetic experiments. They also determined that the magnetite carried the primary component. The ordering temperature of goethite is 120 °C (Table 2), so this secondary component can be removed during the earlier steps of thermal demagnetization. Because the remanence carried by magnetite was contaminated with the secondary remanence carried by hematite in thermal demagnetization, separating the primary component from NRM was difficult. When extracting a primary component one needs a method to remove the hematite beforehand. RCD performed well for this reason, as shown in Fig. 8, as hematite and goethite were removed. Because high coercivity components were demagnetized via RCD, the subsequent AF demagnetization entirely demagnetized the primary magnetization component (Fig. 9c). The present study provides a framework for demagnetization in paleomagnetic studies that have difficulties in separating primary components from secondary CRM.

Conclusions

We devised a new method of demagnetization for paleomagnetic studies, which we call reductive chemical demagnetization (RCD). RCD was performed using a reductive etchant comprised of ascorbic acid solution buffered with sodium bicarbonate. The pH of the etchant was adjusted to a near-neutral value in the region of pH-pE equilibrium diagram in which iron is soluble as ferrous ion. The demagnetized component is greatest at a concentration of 5% ascorbic acid solution, but a range of concentrations between 5 and 20% is effective in the RCD process. Dripping the etchant on a sample is more effective than the conventional technique of dipping the sample in the etchant. The results of rock magnetic experiments show that RCD is effective in demagnetizing both the high coercivity remanence of goethite and high coercivity and high unblocking-temperature remanence carried by hematite. For the reef limestone samples of the Ryukyu Group, the paleomagnetic demagnetizations to extract the primary remanence from NRM were improved via the RCD treatment. The RCD treatment can provide more effective removal of secondary magnetization in paleomagnetic studies of sedimentary rocks.

Abbreviations

RCD: reductive chemical demagnetization; CRM: chemical remanent magnetization; IRM: isothermal remanent magnetization; NRM: natural remanent magnetization; AF demagnetization: alternating field demagnetization.

Authors' contributions

Chisato Anai conducted all of the experiments and wrote the manuscript. Nobutatsu Mochizuki assisted in the rock magnetic experiments and drafting the manuscript. Hidetoshi Shibuya assisted in constructing the framework of this study and manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

Availability of data and materials

Please contact author for data requests.

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