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Blaubeuren, Cloppenburg, and Machtenstein—Three recently recognized H-group chondrite finds in Germany with distinct terrestrial ages and weathering effects

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Abstract–In the last 7 years, three meteorites (Blaubeuren, Cloppenburg, and Machtenstein) found in Germany were identified as chondrites. Two of these rocks had been recovered from the impact sites decades ago but were not considered to be meteorites. The aim of this study is to fully characterize these three meteorites. Based on the compositional data on the silicates, namely olivine and low-Ca pyroxene, these meteorites fit nicely within the H-group ordinary chondrites. The brecciated texture of Blaubeuren and Cloppenburg (both H4-5) is perfectly visible, whereas that of Machtenstein, officially classified as an H5 chondrite, is less obvious but was detected and described in this study. Considering chondrites in general, brecciated rocks are very common rather than an exception. The bulk rock degree of shock is S2 for Blaubeuren and Machtenstein and S3 for Cloppenburg. All samples show significant features of weathering. They have lost their original fusion crust and more than half (W3) or about half (W2-3) of their original metal abundances. The oxygen isotope compositions of the three chondrites are consistent with those of other H chondrites; however, the Cloppenburg values are heavily disturbed and influenced by terrestrial weathering. This is supported by the occurrence of the very rare hydrated iron phosphate mineral vivianite ($Fe^{2+}Fe^{2+}_2[PO_4]_2 \cdot 8H_2O$), which indicates that the chondrite was weathered in a very wet environment. The terrestrial ages of Blaubeuren (~9.2 ka), Cloppenburg (~5.4 ka), and Machtenstein (~1.8 ka) show that these chondrites are very similar in their degree of alteration and terrestrial age compared to meteorite finds from relatively wet terrestrial environments. They still contain abundant metal, although, as noted, the oxygen isotope data indicate substantial weathering of Cloppenburg. The bulk compositions of the three meteorites are typical for H chondrites, although terrestrial alteration has slightly modified the concentrations, leading in general to a loss of Fe, Co, and Ni due to preferential alteration of metals and sulfides. As exceptions, Co and Ni concentrations in Machtenstein, which has the shortest terrestrial age, are typical for H chondrites. The chemical data show no enrichments in Ba and Sr, as is often observed in different meteorite groups of desert finds.

INTRODUCTION

Every year people all over the world collect thousands of rock samples that they believe to be valuable meteorites. To confirm their origin, many of such samples are sent to experts or science institutions for testing. Most of these rocks are terrestrial in origin: They are typically basalts, artificial slags, magnetites, iron ores, flint pieces, ferrous concretions, manganese nodules, or rusty objects such as artificially produced tools or relicts from war.

However, very rarely real meteorites are among the objects found. In the last 7 years, three rocks tested in Germany have been proven to be true meteorites (Blaubeuren, Cloppenburg, and Machtenstein; Figs. 1 and 2) (The Meteoritical Bulletin, 2021). Two of these rocks had been discovered and displaced from their original impact site a long time ago, but at the time the finders did not think they were meteorites. Also, over the last decade, four meteorite falls have been recorded in Germany (Braunschweig, Stubenberg, Renchen, and Flensburg; Bartoschewitz et al., 2017; Bischoff, Barrat, et al., 2017; Bischoff, Barrat, et al., 2019; Bischoff et al., 2021).

While Flensburg was the 33rd recovered meteorite fall in Germany (excluding the unclassified/lost falls of Stolzenau [1647], Ortenau [1671], and Rodach [1775], which are listed in the Meteoritical Bulletin Database), the latest identified Blaubeuren meteorite was the 19th recorded meteorite find. Blaubeuren, at 30.67 kg, is the largest stony meteorite ever detected in Germany. By contrast, the overall single largest meteorite from Germany that is still preserved is the 80 kg iron meteorite Unter-Mässing, found in 1920.

The official classifications of the three chondrites were performed at the Mineralogical State Collection in Munich (Machtenstein) and at the Institut für Planetologie of the University of Münster (Blaubeuren, Cloppenburg) as presented in The Meteoritical Bulletin (2021).

The first scientific details on Machtenstein were published by Hochleitner et al. (2015) and Hoffmann et al. (2015), while the finding circumstances were reported by Heinlein (2014, 2016). The first preliminary results on Cloppenburg were presented by Storz et al. (2017), Li et al. (2017), and Storz (2017) and reports concerning the find circumstances of Blaubeuren were published by Heinlein (2020) and Köhler (2020).

Previously, chemical data for Blaubeuren and Cloppenburg presented in The Meteoritical Bulletin (2021) were obtained for olivine and pyroxene using a scanning electron microscope (SEM). Other detailed studies, including identifying the compositions of other minerals, were not performed. Thus, in this study, we examined the compositions of the main and minor phases of the three chondrites Blaubeuren, Cloppenburg, and Machtenstein using electron microprobe and complemented this with data on the bulk chemical and O isotope composition as well as with data on the density, and selected cosmogenic radionuclide concentrations yielding terrestrial ages.

SAMPLES AND ANALYTICAL PROCEDURES

Several thin and thick sections of Cloppenburg (PL17222, PL17223, PL17224; total area ~410 mm^2), Blaubeuren (PL20057, PL20058, PL20059; total area: ~480 mm^2) from the Institut für Planetologie (Münster), and Machtenstein (~60 mm^2; sample of the Mineralogical State Collection in Munich) were studied by optical and electron optical microscopy. A ZEISS polarizing microscope (Axiophot) was used for optical microscopy in transmitted and reflected light.

A JEOL 6610-LV electron microscope (SEM) at the Interdisciplinary Center for Electron Microscopy and Microanalysis (ICEM) at the University of Münster was used to study the meteorites' fine-grained textures and to identify the different mineral phases. The INCA analytical program provided by Oxford Instruments was used for these energy-dispersive X-ray spectroscopy analyses.

Quantitative mineral analyses were obtained by new microprobe analyses using the JEOL JXA 8530F electron microprobe (EPMA) at the Institut für Mineralogie in Münster, which was operated at 15 kV and a probe current of 15 nA. Natural and synthetic standards were used for wavelength-dispersive spectrometry. As standards for mineral analyses, we used jadeite (Na), kyanite (Al), sanidine (K), chromium oxide (Cr), San Carlos olivine (Mg), hypersthene (Si), diopside (Ca), rhodonite (Mn), rutile (Ti), fayalite (Fe), apatite (P), celestine (S), Co-metal (Co), and nickel oxide (Ni). Considering the Co concentrations, a correction for the interference between the FeK_{β} and the CoK_{α} peak was performed.

Bulk Chemical Analyses

Bulk samples of about 0.5 g from all three meteorites were crushed and homogenized, and about 110 mg was used for analyses at the University of Brest. The chemical compositions of the bulk samples were obtained from the subsamples using inductively coupled plasma atomic emission spectrometry (ICP-AES; for Al, Fe, Mn, Mg, Na, Cr, Co, and Ni) and inductively coupled plasma sector field mass spectrometry (ICP-SFMS). Details are given by Barrat et al. (2012, 2015, 2016). The concentration reproducibility is generally much better than 5% at the chondritic level.

Fig. 1. Locations of the 33 meteorite falls and 19 finds in Germany until 2021 excluding the unclassified/lost falls of Stolzenau (1647), Ortenau (1671), and Rodach (1775), which are listed in the Meteoritical Bulletin Database. Topographic data based on DGM1000 (https://gdz.bkg.bund.de/index.php/default/digitale-geodaten/digitale-gelandemodelle/digitales-gelandemodell-gitterweite-1000-m-dgm1000.html) provided by the BKG and published under the dl-de/by-2-0 data license (https://www.govdata.de/dl-de/by-2-0). (Color figure can be viewed at wileyonlinelibrary.com.)

Oxygen Isotope Analyses

The oxygen isotope compositions of bulk materials of the Blaubeuren, Cloppenburg, and Machtenstein meteorites were analyzed by means of laser fluorination in combination with gas source mass spectrometry (for analytical details, see Pack et al., 2016; Peters et al., 2020; cf. Herwartz et al., 2014; Pack & Herwartz, 2014; Pack et al., 2017). Individual chips were analyzed in three different sessions. The $\delta^{17}O$ and $\delta^{18}O$ are reported on the Vienna Standard Mean Ocean Water (VSMOW) scale, and the $\Delta'^{17}O$ is defined as

$$\Delta'^{17}O = 1000\ \ln\left(\frac{\delta^{17}O}{1000}+1\right) - 0.528 \times 1000\ \ln\left(\frac{\delta^{18}O}{1000}+1\right)$$

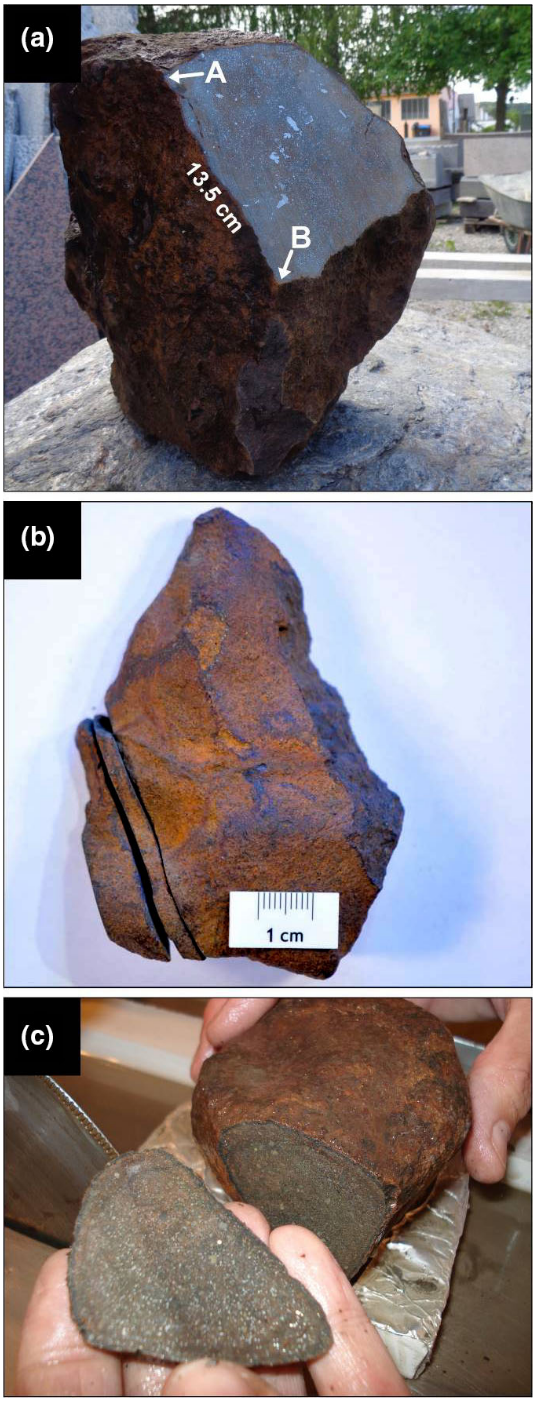

Fig. 2. Images of the three meteorite finds. a) Main mass (29.4 kg) of Blaubeuren; the distance between (A) and (B) is 13.5 cm. b) Cloppenburg after being cut for sample selection for studies. c) Main mass of Machtenstein after initial cutting, where the longest dimension of the end cut is 6.2 cm. (Color figure can be viewed at wileyonlinelibrary.com.)

To anchor $\delta^{17}O$ on the VSMOW scale, we used a $\Delta'^{17}O$ value for San Carlos olivine of 0.052‰ (average value of Pack et al., 2016; Sharp et al., 2016; Wostbrock et al., 2020).

Density Determination

The bulk densities of the pieces of Blaubeuren, Cloppenburg, and Machtenstein were determined in Augsburg with the method described by Consolmagno et al. (2008) using 40 μm diameter glass beads (Table 1).

Cosmogenic Radionuclides and Terrestrial Age Determination

The cosmogenic radionuclides ^{14}C and ^{10}Be were measured by accelerator mass spectrometry (AMS). Using the technique described by Jull et al. (2008, 2010), ^{14}C was detected on homogenized bulk aliquots of Blaubeuren (87 mg), Cloppenburg (60 mg), and Machtenstein (100 mg) at the University of Arizona AMS Laboratory. Aliquots of Blaubeuren (104 mg of 380 mg powder), Cloppenburg (104 mg of 545 mg powder), and Machtenstein (38.5 mg) were radiochemically treated (using a ^{9}Be carrier solution) to produce BeO (Merchel & Herpers, 1999), which thereby allowed for $^{10}Be/^{9}Be$ measurements at the Helmholtz-Zentrum Dresden-Rossendorf (Akhmadaliev et al., 2013). Beryllium-10 was normalized to the in-house standard SMD-Be-12 and transformed into specific activity units of disintegrations per minute (dpm) using the ^{10}Be half-life of (1.387 ± 0.012) Ma (Korschinek et al., 2010).

FIND CIRCUMSTANCES AND HISTORICAL ASPECTS

Blaubeuren

In the garden of his property in Blaubeuren, Hansjörg Bayer was digging a cable trench in 1989. When excavating a cable duct, he found a stone weighing 30.26 kg at 50–70 cm depth, which had an unusually high density and was attracted to a magnet. The finder kept the stone in his garden as a curiosity until 2015, leaving it exposed to weathering. From 2015 to 2020, the stone was kept in dry conditions in the basement of his house until it was finally examined and recognized as a stony meteorite. After the analysis, another meteorite fragment of 410 g was found in the garden, which obviously was broken off from the main piece. The main mass of 29.40 kg is currently with the finder.

Cloppenburg

The rock was found in March 2017 by Hartmut Osterburg, facility manager of a Cloppenburg school, while collecting rocks for the school garden. The broken stone fragment, weighing 141 g, was lying on a rock pile next to a potato field. The finder was curious about it because of its magnetic properties and its unusual

Table 1. Details of the H chondrite finds Blaubeuren, Cloppenburg, and Machtenstein.

	Blaubeuren	Cloppenburg	Machtenstein
Date of find	1989 (2020)[a]	March 15, 2017	1956 (2014)[b]
Total mass (kg)	30.67	0.141	1.422
Classification	H4-5; br	H4-5; br	H5; br
Shock stage	S2	S3	S2
Weathering grade	W3	W3	W2-3
Olivine (Fa)	18.7 ± 0.2	18.8 ± 0.2	18.8 ± 0.3
Pyroxene (Fs)	16.6 ± 0.3	16.5 ± 0.4	16.3 ± 0.7
Pyroxene (Wo)	1.6 ± 0.2	0.8 ± 0.4	1.4 ± 0.9
Plagioclase (An)	12.6 ± 0.4	14.7 ± 8.0	8.8 ± 2.8
$\delta^{17}O$	2.656½	4.054½	2.514½
$\delta^{18}O$	3.963½	6.474½	3.890½
Density (g cm^{-3})	3.34 ± 0.01	3.33 ± 0.03	3.39 ± 0.05
Cosmogenic nuclides and terrestrial ages			
^{14}C (dpm kg^{-1})	14.0 ± 0.4	23.8 ± 0.5	34.4 ± 0.5
^{10}Be (dpm kg^{-1})	17.09 ± 0.33	18.28 ± 0.35	17.13 ± 0.31
T-age (^{14}C)	9.9 ± 1.3 ka	5.5 ± 1.3 ka	2.5 ± 1.3 ka
T-age ($^{14}C/^{10}Be$)	9.2 ± 0.3 ka	5.4 ± 0.3 ka	1.8 ± 0.2 ka

br = breccia; Fa, Fs, Wo in mol%; T-age = terrestrial age.
[a] Blaubeuren was found in 1989 but only recognized as a meteorite in 2020.
[b] Machtenstein was found around 1956 but was only recognized as a chondrite in 2014.

appearance. Immediately after finding the rock, he brought it to the attention of a meteorite specialist of the Institute of Planetary Research at the German Aerospace Centre (Deutsches Zentrum für Luft- und Raumfahrt DLR). The remaining main mass of 117.6 g is kept in the collection of Dieter Heinlein, Augsburg.

Machtenstein

Around 1956, Sepp Landmann, a young Bavarian farmer's son, found an unusual stone while working in his parents' Rennhof field near Dachau. The rock was heavier than the usual reading stones and contained metal. The fist-sized lump, weighing 1422 g, was kept by the finder in the farmhouse. In 1982, Landmann gave the stone to his friend Hans Hartl, who had preserved it for several decades in the front yard of his home in Machtenstein, until it was rediscovered and recognized as a meteorite in spring 2014. The remaining main mass of 1378 g is now presented in the RiesKraterMuseum, Nördlingen.

MINERALOGY, SHOCK METAMORPHISM, AND WEATHERING

In the following paragraphs, we present details concerning the mineralogy of these rocks (Figs. 3–5;

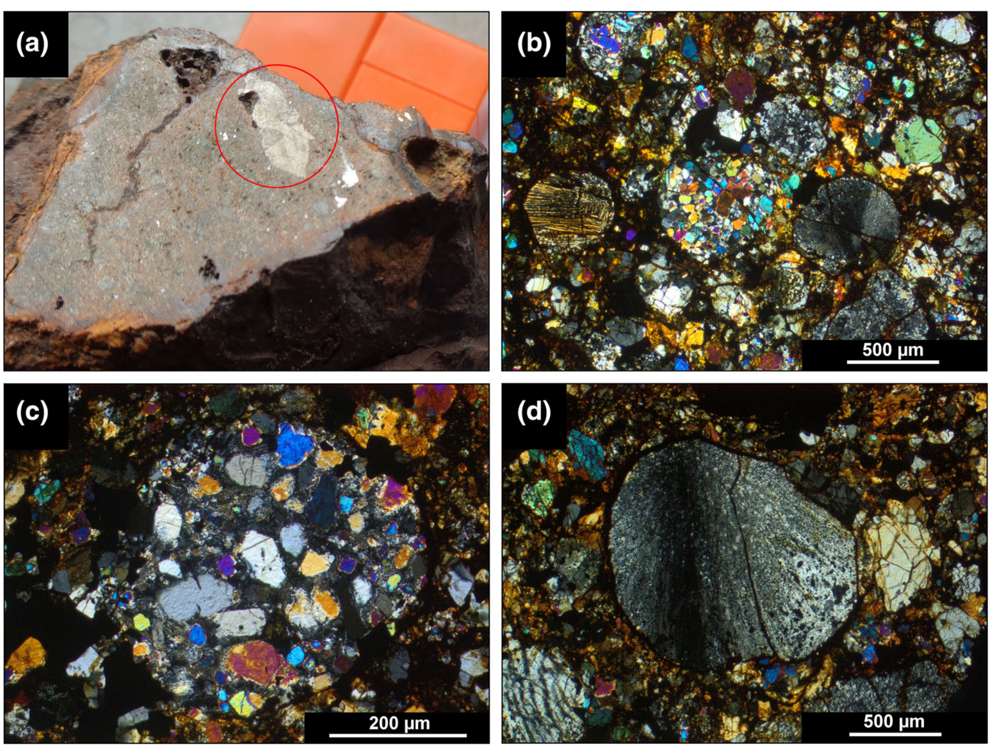

Fig. 3. Typical views of the Blaubeuren chondrite. a) Large FeS-rich aggregate (about 1.2 cm in longest dimension) on the cut surface. b) Typical area of the type 4 lithology of the breccia. c) Recrystallized porphyritic olivine-pyroxene (POP) chondrule. d) Radial pyroxene (RP) chondrule. b–c) Images taken in polarized light, crossed nicols. (Color figure can be viewed at wileyonlinelibrary.com.)

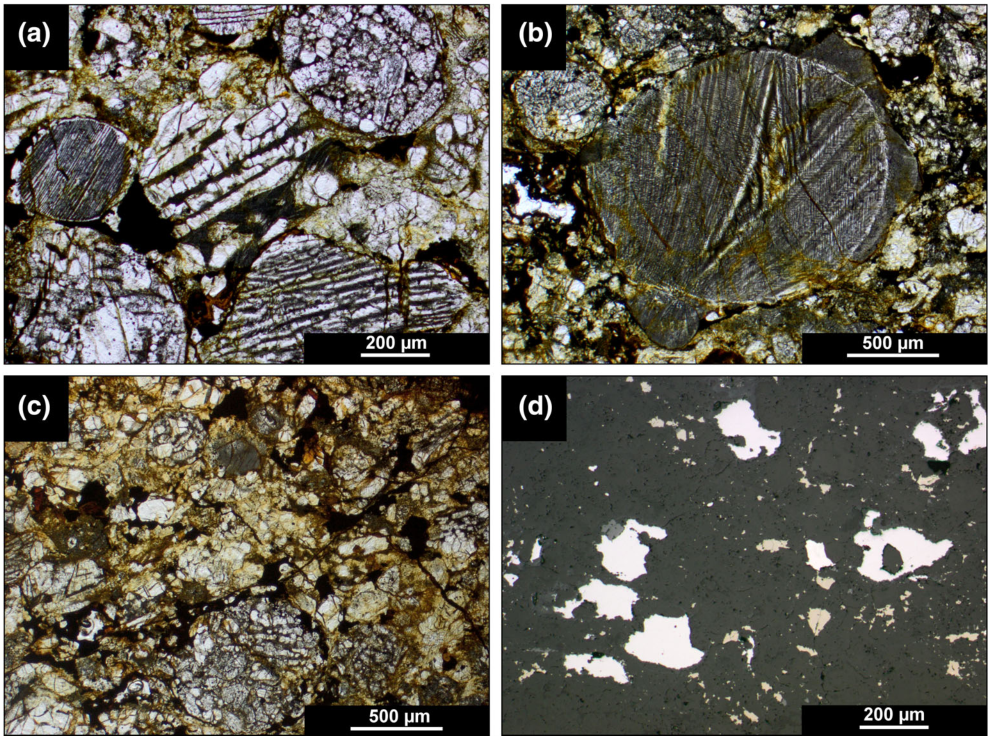

Fig. 4. Typical areas of the Cloppenburg chondrite. a) The chondritic texture is well preserved. b) A large compound chondrule consisting of at least six attached subchondrules (siblings). c) Typical appearance of a fragment of petrologic type 5. All three images (a–c) in plane polarized light. d) Reflected light image showing an interior area of Cloppenburg with well-preserved metals. (Color figure can be viewed at wileyonlinelibrary.com.)

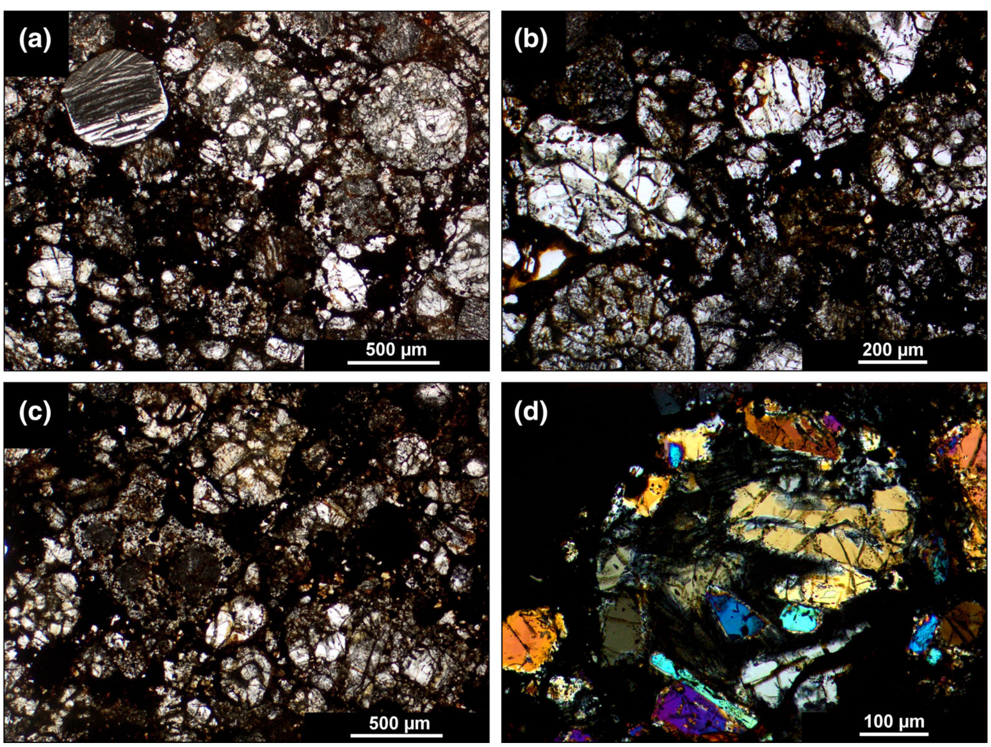

Fig. 5. Typical images in polarized light from Machtenstein: In some areas (a, b), the chondritic texture is well preserved, while in other areas (c), such a texture is largely missing; (d) recrystallized porphyritic chondrule (POP; crossed polarizers). (Color figure can be viewed at wileyonlinelibrary.com.)

Table 1), including details on the shock and brecciation features (Fig. 6) and the effects of terrestrial alteration (Fig. 7).

Mineralogy

Blaubeuren (H4-5 Breccia)

The rock lacks a fusion crust due to the consequences of terrestrial weathering. On the cut surface, large aggregates of Fe-sulfide are visible as well as holes (Fig. 3a). The holes are probably also a result of terrestrial modifications. The rock is certainly a breccia, containing fragments of petrologic type 4 and type 5 (Fig. 6) and is very weakly shocked (S2; Stöffler et al., 1991). Within the type 4 fragments, the chondritic texture is well preserved, and intact chondrules can easily be detected (Fig. 3). Due to its residence on Earth, the meteorite is heavily weathered (W3), and most of the metal is oxidized. The remaining metal grains have thick rims of terrestrial alteration products (Fe-oxides and Fe-hydroxides). On the outside, the weathering crust contains contaminants (often quartz grains; Fig. 7b) of the local Earth surface. The bulk density of Blaubeuren was determined to be 3.34 ± 0.01 g cm^{-3} (Table 1).

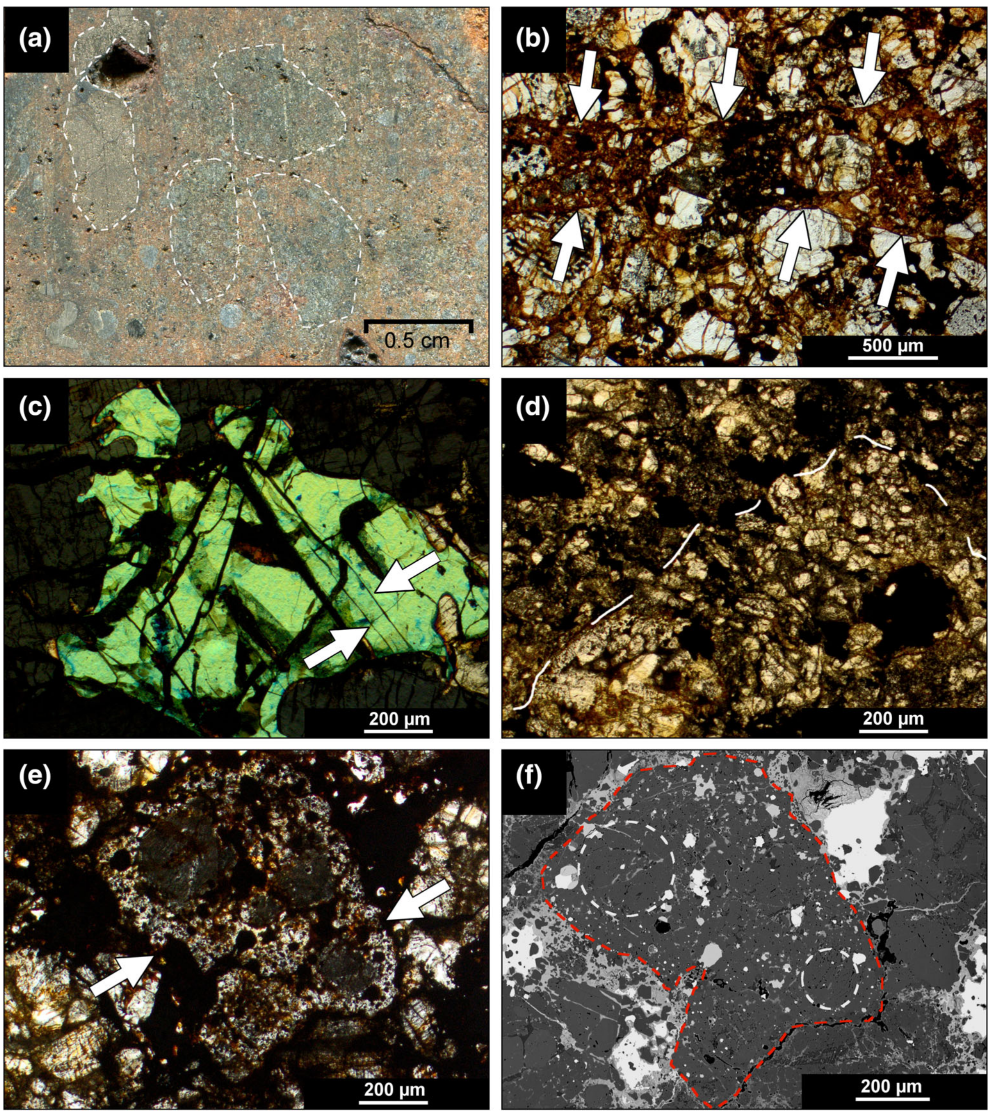

Fig. 6. Brecciation features in (a, b) Blaubeuren, (c, d) Cloppenburg, and (e, f) Machtenstein: On the (a) cut surface, brecciation features are obvious and are nicely visible in transmitted light (b). The boundaries of the clasts are indicated by small arrows. c) Cloppenburg has a shock stage of S3, indicated by planar features in olivine (arrows) in addition to (d) visible boundaries between fragments. e) Brecciation features are minor in Machtenstein, but they exist. One clast (arrows) may be a chondritic fragment; it is shown in detail in (f) as a BSE image. (Color figure can be viewed at wileyonlinelibrary.com.)

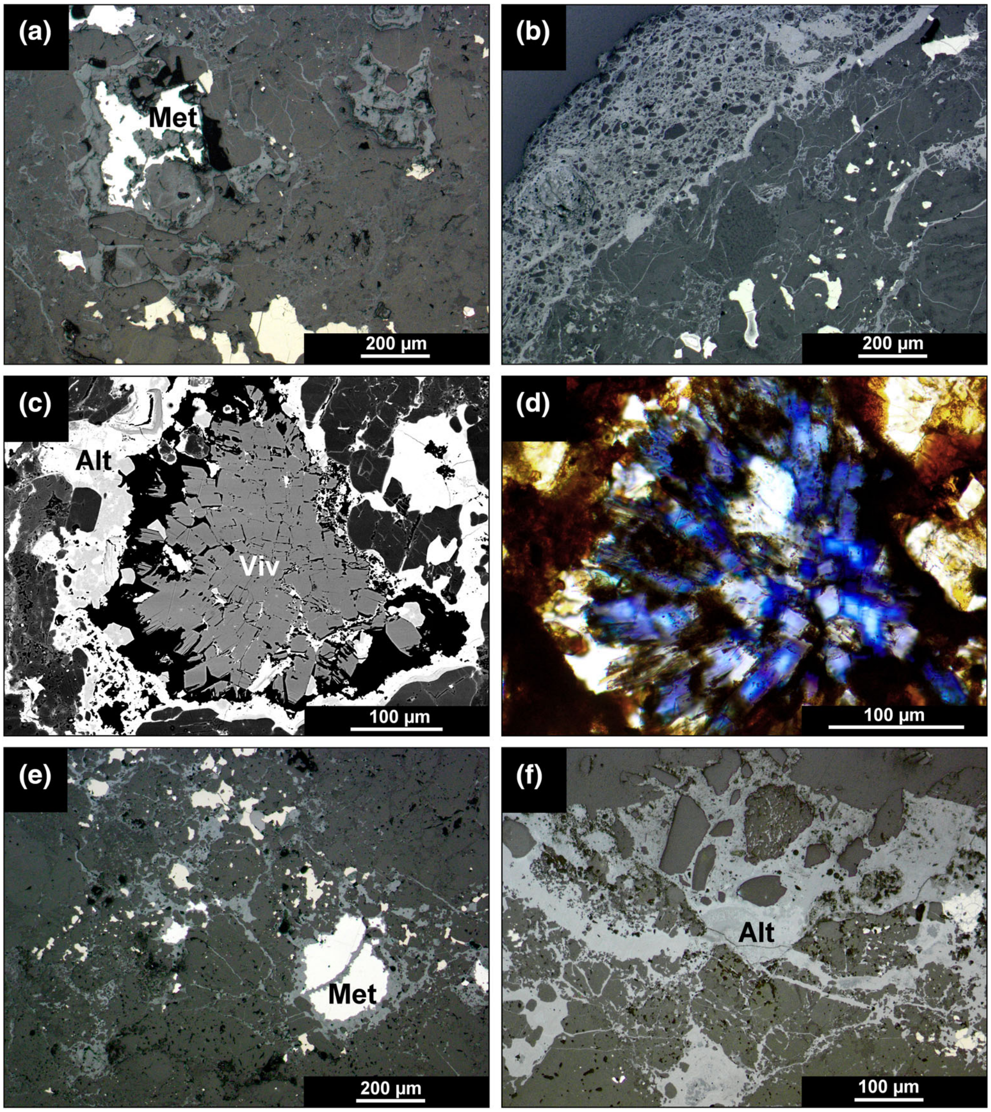

Fig. 7. Weathering effects in (a, b) Blaubeuren, (c, d) Cloppenburg, and (e, f) Machtenstein: Most of the metal (Met) in (a) Blaubeuren has been destroyed, whereas some large grains are still visible in Machtenstein (e). The weathering crust (b, f) often contains terrestrial contaminants, mainly of quartz grains. c) BSE image of vivianite (Viv; Viv appears blue in plane polarized light [d]), which was found in Cloppenburg indicating weathering in a very wet environment. All images (except [c] and [d]) were taken in reflected light. Alt = terrestrial alteration. (Color figure can be viewed at wileyonlinelibrary.com.)

The mean composition of olivine is $Fa_{18.7\pm0.2}$ with a compositional range of $Fa_{18.1-19.0}$. The low-Ca pyroxenes have a mean composition of $Fs_{16.6\pm0.3}$ with a range of $Fs_{16.3-17.0}$ (Table 2). The Na-rich plagioclase has a mean An content of 12.6 $\pm$ 0.4 mol% with a range between 11.8 and 13.1 mol% (Table 2). Other analyzed phases include phosphates (merrillite and Cl-apatite) and chromite (Table 3), as well as troilite and metals (Table 4). The Cl-apatites have on average a Cl concentration of 3.9 wt% with a range of 3.2–4.3 wt%. The Na_2O concentration of merrillite is very uniform and varies between 2.6 and 2.8 wt% (mean: 2.66 wt%). The chromites have Cr_2O_3 concentrations between 55.4 and 57.5 wt% (mean: 56.5 wt%). Compositions of metals and sulfides are given in Table 4. The kamacites have a mean Co and Ni concentration of 0.47 and 6.4 wt%, respectively.

Cloppenburg (H4-5 Breccia)

Texturally and mineralogically, Cloppenburg is very similar to Blaubeuren. The rock is also a breccia, containing fragments of petrologic type 4 and 5 (Figs. 4 and 6). Within the type 4 domains, the chondritic texture is well preserved (Fig. 4a), and one of its

Table 2. Chemical composition of the main silicates within Blaubeuren, Cloppenburg, and Machtenstein.

	Blaubeuren			Cloppenburg			Machtenstein		
	Olivine	Pyroxene	Plagioclase	Olivine	Pyroxene	Plagioclase	Olivine	Pyroxene	Plagioclase
n	10	10	10	10	10	10	10	10	10
SiO_2	38.6	56.0	64.6	38.7	56.1	64.0	38.8	56.0	66.0
TiO_2	<0.02	0.17	0.04	<0.03	0.10	0.05	<0.02	0.12	<0.03
Al_2O_3	n.d.	0.18	21.1	<0.01	0.14	21.4	<0.01	0.31	20.4
Cr_2O_3	<0.02	0.14	<0.02	<0.02	0.14	<0.01	<0.01	0.20	<0.02
FeO	17.6	11.2	0.70	17.6	11.1	0.81	17.7	11.0	0.59
MnO	0.48	0.51	<0.02	0.47	0.48	<0.01	0.47	0.47	<0.02
MgO	43.0	30.9	<0.01	42.6	31.3	<0.03	42.8	31.1	0.09
CaO	<0.01	0.82	2.61	0.00	0.42	3.0	0.01	0.74	1.83
Na_2O	<0.01	<0.02	9.4	<0.02	<0.01	9.3	n.d.	<0.01	10.0
K_2O	<0.01	<0.01	0.93	<0.01	n.d.	0.61	n.d.	<0.01	0.77
Total	99.75	99.95	99.43	99.46	99.79	99.22	99.82	99.96	99.75
Fa	18.65 ± 0.22			18.80 ± 0.18			18.85 ± 0.26		
Fs		16.63 ± 0.22			16.45 ± 0.39			16.30 ± 0.72	
Wo		1.57 ± 0.20			0.79 ± 0.39			1.41 ± 0.88	
An			12.55 ± 0.38			14.69 ± 7.98			8.77 ± 2.83
Or			5.33 ± 0.62			3.50 ± 1.44			4.43 ± 1.61

Chemical concentrations in wt%; Fa, Fs, Wo, An, Or in mol%; n.d. = not detected.

Table 3. Chemical composition of chromites and phosphates within Blaubeuren, Cloppenburg, and Machtenstein.

	Blaubeuren			Cloppenburg			Machtenstein	
	Chromite	Cl-Apatite	Merrillite	Chromite	Cl-Apatite	Merrillite	Chromite	Merrillite
n	8	6	4	5	1	5	5	6
SiO_2	0.05	0.64	0.06	0.18	0.16	1.27	0.04	0.03
TiO_2	1.57	n.d.	n.d.	1.67	n.d.	n.d.	2.03	n.d.
Al_2O_3	6.7	0.08	n.d.	6.4	<0.02	0.06	6.3	n.d.
Cr_2O_3	56.5	<0.02	<0.02	56.0	<0.03	<0.02	56.5	<0.02
FeO	29.1	2.41	0.64	29.6	0.81	3.3	29.3	0.76
MnO	0.95	<0.03	<0.03	1.00	<0.04	0.05	0.92	<0.02
MgO	2.67	<0.02	3.5	2.64	0.03	3.4	2.79	3.6
CaO	<0.01	51.0	45.9	0.04	53.0	42.9	n.d.	45.8
Na_2O	n.d.	0.23	2.66	n.d.	0.28	2.58	n.d.	2.64
K_2O	n.d.	n.d.	0.07	n.d.	n.d.	0.06	n.d.	0.04
P_2O_5	n.d.	40.1	45.6	n.d.	37.7	43.7	n.d.	46.3
Cl	n.d.	3.9	n.d.	n.d.	3.4	n.d.	n.d.	n.d.
Total	97.55	98.43	98.48	97.53	95.47	97.34	97.88	99.21

All data in wt%; n.d. = not detected.

Table 4. Chemical composition of representative metals (Kam = kamacite, Taen = taenite, Tetratae = tetrataenite) and troilite (Troi) within Blaubeuren, Cloppenburg, and Machtenstein.

	Blaubeuren				Cloppenburg				Machtenstein		
	Kam	Taen	Tetratae	Troi	Kam	Taen	Tetratae	Troi	Kam	Taen	Troi
wt%	*n* = 13	*n* = 9	*n* = 2	*n* = 13	*n* = 11	*n* = 1	*n* = 7	*n* = 4	*n* = 13	*n* = 7	*n* = 15
Fe	93.1	66.8	50.1	62.8	91.8	67.2	50.9	62.5	92.5	66.3	63.4
Ni	6.4	31.9	49.1	0.18	6.4	32.3	47.2	0.12	7.1	32.2	<0.02
Co	0.47	0.12	0.07	<0.02	0.50	0.10	0.08	<0.01	0.52	0.13	n.d.
S	n.d.	n.d.	n.d.	36.2	n.d.	n.d.	n.d.	36.1	n.d.	<0.02	36.5
Cr	n.d.	<0.01	n.d.	<0.01	<0.01	<0.03	<0.02	<0.01	<0.02	<0.01	<0.02
Mn	n.d.	<0.01	n.d.	n.d.	n.d.	n.d.	<0.01	<0.01	n.d.	<0.01	<0.01
Total	99.97	98.84	99.27	99.21	98.71	99.63	98.21	98.75	100.14	98.67	99.95

All data in wt%; n.d. = not detected.

chondrules contains many siblings, similar to the multicompound chondrule ACC from Allende (Bischoff, Wurm, et al., 2017). The planar fractures in olivine indicate that the breccia is weakly shocked (S3; Fig. 6c). Shock veins are present but rare. In general, the meteorite is heavily weathered and most metal is replaced by weathering products (W3). Only within the interior, some areas still show well-intact metals (Fig. 4d). In Cloppenburg, an aggregate of vivianite (a water-bearing Fe-phosphate; Figs. 7c and 7d) occurs, which is a very rare secondary mineral in meteorite finds (see below). Cloppenburg has a density of 3.33 ± 0.03 g cm^{-3} (Table 1). The newly performed analyses reveal that the mean composition of olivine is $Fa_{18.8\pm0.2}$ with a compositional range of $Fa_{18.6–19.2}$ (Table 2). The low-Ca pyroxenes have a mean composition of $Fs_{16.5\pm0.4}$ with a range of $Fs_{15.4–16.9}$ (Table 2). Other phases that were identified and analyzed include plagioclase, chromite, phosphates (merrillite, Cl-apatite), troilite, and metals. The analyzed plagioclases have a mean An content of 14.7 mol%, showing a remarkable range in composition ($An_{8–32}$). Rubin (1992) also reported compositionally variable plagioclase in ordinary chondrites and considered to be due to shock metamorphism. The only single measured Cl-apatite has a Cl concentration of 3.4 wt%, while the Na_2O concentration of merrillite varies between 2.3 and 2.7 wt% (mean: 2.58 wt%). The chromites have a mean Cr_2O_3 concentration of 56.0 wt% varying between 55.4 and 57.5 wt% (Table 3). Among the troilites and metals (Table 4), the kamacites have a mean Co and Ni concentration of 0.50 and 6.4 wt%, respectively. In Cloppenburg, Ni-bearing sulfides were also found to have a concentration between 4 and 14 wt% Ni.

Machtenstein (H5 Breccia)

Due to the effects of terrestrial weathering, the rock does not contain any fusion crust. In some areas, Machtenstein has still a preserved chondritic texture (Figs. 5a and 5b) with partly recrystallized chondrules

(Fig. 5d), whereas in other parts of the rock, such a texture is barely visible (Fig. 5c). In general, the rock has a brecciated texture, although the typical features of brecciation are not clearly visible (see below).

The mean composition of randomly analyzed olivine is $Fa_{18.8\pm0.3}$ with a compositional range of $Fa_{18.5–19.5}$ (Table 2). The low-Ca pyroxenes have a mean composition of $Fs_{16.3\pm0.7}$ with a range of $Fs_{14.2-17.1}$. The analyzed plagioclases show a mean An content of 8.8 ± 2.8 mol% varying from 3.5 to 12.0 mol% An. Other phases that were identified and analyzed include chromite, phosphate (merrillite), troilite, and metals. The Na_2O concentration of merrillite varies between 2.4 and 2.8 wt% (mean: 2.64 wt%) and the chromites have Cr_2O_3 concentrations between 55.5 and 57.1 wt% (mean: 56.5 wt%; Table 3). Compositions of metals and sulfides are given in Table 4. The kamacites have a mean Co and Ni concentration of 0.52 and 7.1 wt%, respectively (Table 4). A density of 3.39 ± 0.05 g cm^{-3} was determined for Machtenstein.

SHOCK METAMORPHISM AND BRECCIATION

All three chondrites are very weakly (S2) or weakly (S3) shocked (Bischoff & Stöffler, 1992; Stöffler et al., 1991). Since all three chondrites are breccias (Fig. 6), the shock stage of the lowest shocked fragment defines the overall shock degree of the individual bulk chondrites. In the very weakly shocked samples of Blaubeuren and Machtenstein, olivine shows undulatory extinction (both S2). Within the Cloppenburg meteorite, planar deformation features in olivine are an obvious indication for a shock degree of S3 (Fig. 6c). Different clasts are clearly visible on the cut surface of Blaubeuren as well as in thin sections (Figs. 6a and 6b). Similarly, boundaries of clasts are also observed in Cloppenburg (Fig. 6d). Brecciation features are not so obvious in Machtenstein. After a detailed optical analysis, the strange fragment-like object in Figs. 6e appears to be a fragment of a different chondrite (Fig. 6f).

WEATHERING

All samples show significant features of weathering and have lost their original fusion crust due to terrestrial modifications. In general, considering the studied thin sections, all three meteorites have lost more than or about half of their original metal abundances (Figs. 7a, 7c, and 7e). However, their interiors do contain some less-altered areas. Such an area within Cloppenburg is shown in Fig. 4d. Also, Machtenstein still contains up to 60% of the original metal in the interior (Fig. 7e), whereas the metal close to the outside has been almost completely transformed into oxides/hydroxides. Massive weathering is frequently observed along cracks in the rocks. Often the weathering crust contains a mixture of weathering products (Fe-rich oxides/hydroxides) and terrestrial contaminants like quartz grains, as shown for Blaubeuren and Machtenstein (Figs. 7b and 7f).

Besides the strong terrestrial transformation of metals into oxides/hydroxides in Cloppenburg, another very rare but spectacular feature of weathering is visible: The formation of vivianite ($Fe^{2+}Fe^{2+}{}_2[PO_4]_2{\cdot}8H_2O$; e.g., Rothe et al., 2014). Vivianite is a hydrated iron phosphate mineral and easily visible due to the intense bluish color in transmitted light. The occurrence of vivianite (Figs. 7c and 7d) indicates that the sample was weathered in a very wet environment.

TERRESTRIAL AGES

For all three H chondrites, we obtained estimates of the terrestrial age from both ^{14}C alone and combined $^{14}C/^{10}Be$ measurements. The latter is more accurate, since the ^{10}Be concentration corrects for any shielding effects on ^{14}C (Jull, 2006; Jull et al., 2010). The terrestrial ages of Blaubeuren (~9.2 ka), Cloppenburg (~5.4 ka), and Machtenstein (~1.8 ka) are long for chondrites from relatively wet environments still having abundant metal. Details concerning the relevant ^{14}C and ^{10}Be isotopic concentrations are given in Table 1.

OXYGEN ISOTOPES

The oxygen isotope compositions of the three chondrites are given in Table 1 and shown in Fig. 8. The data are consistent with those of other H chondrites; however, the Cloppenburg values are heavily disturbed and influenced by terrestrial weathering (Fig. 8; see discussion).

BULK CHEMISTRY

The bulk chemical compositions of Blaubeuren, Cloppenburg, and Machtenstein are given in Table 5. The concentrations of most elements are consistent with those of other H chondrites (Lodders & Fegley, 1998). Some values are slightly modified due to terrestrial alteration as discussed below.

DISCUSSION

Classification of the Rocks

The newly obtained compositional data on the silicates in this study are in excellent agreement with the

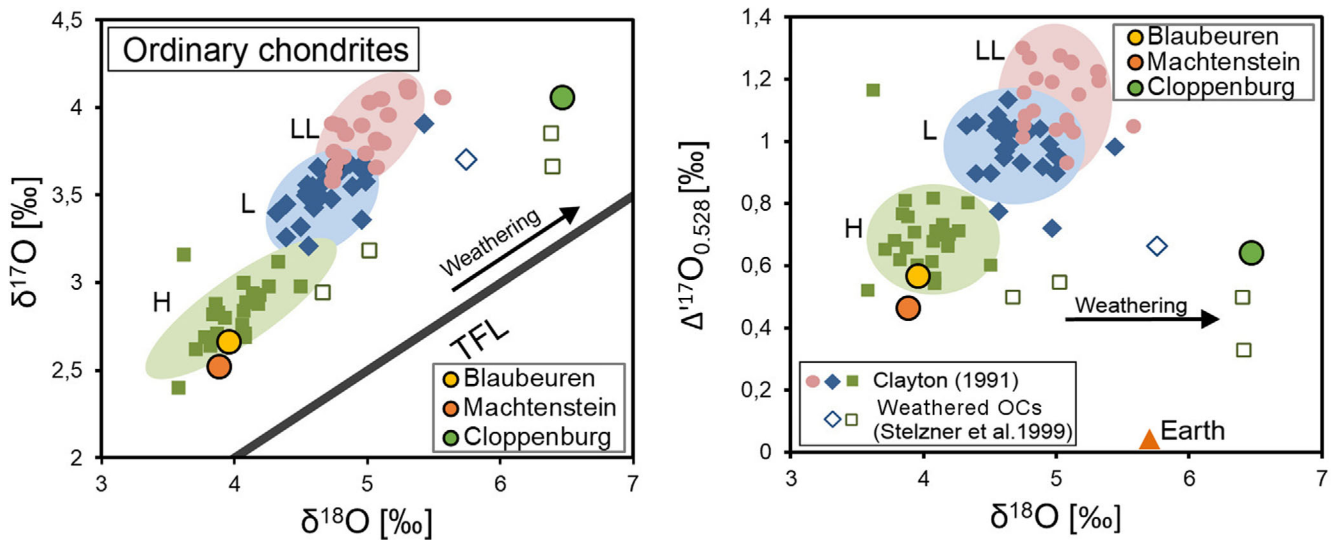

Fig. 8. The oxygen isotope compositions of the three chondrites Blaubeuren, Cloppenburg, and Machtenstein. For comparison, we include data for other relatively fresh chondrites (Clayton et al., 1991) and terrestrially weathered chondrites (Stelzner et al., 1999). The effects of terrestrial weathering are clearly visible for Cloppenburg. (Color figure can be viewed at wileyonlinelibrary.com.)

results obtained for the initial classification of these meteorites (Storz, 2017; Storz et al., 2017; The Meteorite Bulletin, 2021). The mean compositions of olivine, low-Ca pyroxene, and kamacite fit excellently within the field for H-group ordinary chondrites (e.g., Rubin, 1990). The brecciated texture of Blaubeuren and Cloppenburg is perfectly visible. Based on the different degrees of recrystallization of neighboring clasts, an H4-5 classification of both breccias is appropriate. The features of brecciation in Machtenstein are not as obvious as in the other two, but they exist. The Machtenstein meteorite is classified as an H5 chondrite (Hochleitner et al., 2015; Hoffmann et al., 2015; The Meteorite Bulletin Database). Here, we classify the rock as an H5 breccia, although some areas of the rock show a well-preserved chondritic texture (Figs. 5a and 5b) indicating less recrystallization than typical type 5 chondrites (our suggestion: H4/5).

Considering the oxygen isotopic compositions of the three chondrites, interesting differences can be reported: The O isotope data of Blaubeuren and Machtenstein perfectly plot within the field for H chondrites (e.g., Clayton et al., 1976), while the data for Cloppenburg represent significantly higher values of $\delta^{17}O$ and $\delta^{18}O$. Since all mineralogical data indicate that Cloppenburg is an H chondrite, this effect can only be explained by terrestrial weathering. As shown above, this alteration was likely accompanied with the formation of vivianite ($Fe^{2+}Fe^{2+}{}_2[PO_4]_2{\cdot}8H_2O$). The presence of vivianite (Figs. 7c and 7d), a hydrated iron phosphate mineral, indicates that the sample was weathered in a very wet environment, consistent with the find location in Lower Saxony having abundant moors.

The Bulk Compositions and the Effects of Weathering

The chemical compositions of all three meteorites indicate an H chondrite heritage. The concentrations of most elements are consistent with those of other H chondrites, as published by Lodders and Fegley (1998). Although the samples spent a long time on Earth, the data show no enrichments in Ba and Sr, as is typically observed in different groups of desert finds (e.g., Ebert et al., 2019; Llorca et al., 2013; Stelzner et al., 1999). Still, since they are finds, terrestrial alteration has slightly modified the original bulk compositions of all three meteorites. Remarkable differences can be seen regarding the main siderophile elements. In all three chondrites, the Fe concentrations are lower than in meteorite falls (Table 4); similar trends were observed for Ni and Co in Blaubeuren and Cloppenburg. This is probably due to the destruction of metals and sulfides, which was already observed by Stelzner et al. (1999), who studied the weathering effects in ordinary chondrites from the Acfer region in the Sahara. They found that Fe, Ni, and Co are partly flushed from the meteorites as the metal oxidation proceeds. However, it has to be considered that the degree of this effect is certainly related to the sampling depths of the analyzed material. Concerning the three H chondrites from our study, the sampling depths are quite well known and similar, that is, Cloppenburg ~4 mm, Blaubeuren and Machtenstein, both ~5 mm. Hence, we can argue for a relationship between the loss of certain

Table 5. Trace and major element bulk compositions of Blaubeuren, Machtenstein, and Cloppenburg.

Element	Blaubeuren H5-6	Machtenstein H5, br	Cloppenburg H4-5	H chondrites Mean
Na	0.25*	0.35*	0.19*	0.61*
Mg	13.28*	13.25*	12.79*	14.1*
Al	1.05*	1.05*	0.95*	1.06*
P	812	861	1450	1200
K	421	340	667	780
Ca	1.02*	1.11*	0.93*	1.22*
Ti	480	528	577	630
Cr	3597	3564	4139	3500
Mn	2036	2045	2500	2340
Fe	24.5*	23.8*	23.5*	27.2*
Co	621	744	635	830
Ni	1.57*	1.69*	1.38*	1.71*
Traces				
Li	2.41	2.22		1.7
Be	0.027	0.028		0.030
Sc	7.39	7.34	8.03	7.8
V	49.4	50.7	78.8	73
Zn	25.6	26.0	46.8	47
Ga	4.46	3.38	4.55	6.0
Rb	1.17	0.23	1.65	2.3
Sr	5.58	7.23	6.75	8.8
Y	1.65	1.90	2.14	2.0
Zr	4.47	4.50	5.96	7.3
Nb	0.399	0.407	0.479	0.4
Cs		0.011	0.022	
Ba	2.06	2.72	4.00	4.4
La	0.226	0.284	0.368	0.301
Ce	0.599	0.750	0.915	0.763
Pr	0.089	0.111	0.134	0.120
Nd	0.450	0.548	0.653	0.581
Sm	0.147	0.175	0.205	0.194
Eu	0.0641	0.0576	0.0730	0.074
Gd	0.204	0.240	0.271	0.275
Tb	0.0348	0.0441	0.0505	0.049
Dy	0.262	0.301	0.339	0.305
Ho	0.0586	0.0673	0.0754	0.074
Er	0.174	0.199	0.223	0.213
Tm	0.0270	0.0307		0.033
Yb	0.178	0.203	0.219	0.203
Lu	0.0274	0.0314	0.0328	0.033
Hf	0.135	0.134	0.149	0.150
Ta	0.0163	0.0191	0.0228	0.021
W	0.154	0.186		0.164
Pb	0.0119	0.0886	0.0485	0.240
Th	0.0308	0.0353	0.0485	0.038
U	0.0080	0.0106	0.0189	0.013

Data for Cloppenburg are from Bischoff, Barrat, et al. (2019). The mean H chondrite data are from Lodders and Fegley (1998).
*Data in wt%; other data in ppm.

elements (Ni and Co) and the terrestrial age: Machtenstein with the shortest terrestrial age and the lowest degree of weathering (W2-3) has lost less Ni and Co than Blaubeuren and Cloppenburg (Table 4). The volatile elements Na, K, and P also suffered modifications in the terrestrial environment. In most cases, a significant decrease can be diagnosed. However, in Cloppenburg, a small gain of P is found probably related to the formation of the phosphate vivianite in the wet environment (see above; Fig. 7).

The Terrestrial Ages and Weathering of Meteorites

As mentioned above, the terrestrial ages of Blaubeuren (~9.2 ka), Cloppenburg (~5.4 ka), and Machtenstein (~1.8 ka) are surprisingly long for chondrites from wet Central Europe that still have abundant metal, although all samples show considerable weathering effects. The related degrees of weathering are given as W3 for Blaubeuren and Cloppenburg and W2-3 for Machtenstein. The W3 classification (Wlotzka, 1993) indicates that more than half of a meteorite's original metals has been transformed into oxides/hydroxides, although metal-rich areas in the interior can locally be observed, like in Cloppenburg (Fig. 4d). The occurrence of the rarely observed alteration product vivianite in Cloppenburg indicates that the sample was weathered in a very wet environment, consistent with the find location in Lower Saxony. Within these kinds of wet and reducing conditions, the meteorite was likely better conserved, explaining the preservation of metals, even though its terrestrial age is relatively long. For Machtenstein (W2-3), the interiors still have most of the primary metals (Fig. 2c), and only in the outer areas have more than half of the original metals been altered into oxides/hydroxides (Fig. 7f). This finding roughly agrees with the sequence of the terrestrial ages (Blaubeuren > Cloppenburg > Machtenstein).

As expected, the ages are higher for desert finds for a similar degree of aqueous alteration. All desert chondrites with a degree of aqueous alteration >W3 have at least a terrestrial age of 13 ka, while some W2 chondrites (Acfer 023 and Acfer 178) even have a terrestrial age over 20 ka (Stelzner et al., 1999; Wlotzka et al., 1995). Jull et al. (2010) found much more variability of weathering grade with terrestrial age in Western Australian meteorites. Although most meteorites in that collection with W3 are also older, there were a few exceptions. Bland et al. (2000) showed a relationship between the degree of oxidation and terrestrial age. Similar results were found by Zurfluh et al. (2016), who studied meteorites from Oman, and who also demonstrated that a relationship between the terrestrial age and the degree of weathering exists. Here, we perform a similar approach, considering chondrite finds recovered from temperate environments similar to those of the find sites of the three German chondrites. The data are plotted in Fig. 9.

Analysis of the terrestrial age of the ungrouped enstatite meteorite Zakødzie (Poland) revealed that this rock is the youngest, as it is a relatively fresh meteorite find (recent fall; Patzer et al., 2002), whereas Lake House (H5, England) is the oldest considered rock, with a terrestrial age of 34 ± 12 ka, and it is the most altered rock (W5; Pillinger et al., 2011). The Danebury H5 chondrite (England) has a relatively short terrestrial age (2.6 ± 1.3 ka) and also shows a low degree of terrestrial alteration (W1/2; Pillinger et al., 2014). Considering all these data in Fig. 9, the location at which the classified specimen is sampled must be considered. This is uncertain in many cases, but we assume that recovered meteorite finds have mostly been cut at the edge and not through their cores, similar to the sampling process for Blaubeuren, Cloppenburg, and Machtenstein, as shown in Fig. 2. As shown in Fig. 9, the chondrites Blaubeuren, Cloppenburg, and Machtenstein are very similar in their degree of alteration and their terrestrial age compared to meteorite finds from other areas in the world that have a similar climate. Thus, their remarkable long terrestrial ages are not exceptional, as previously considered.

Three New Brecciated Chondrite Finds and the Abundance of Breccias Among Chondrites

All three H chondrites are breccias, which is remarkable considering the following observations: Bischoff, Schleiting, et al. (2018) and Bischoff, Schleiting, et al. (2019) studied the shock and brecciation effects of 2280 chondrites and found that 23% (276 of 1193) of the H chondrites, 23% (220 of 947) of the L chondrites, and 79% (110 of 140) of the LL chondrites are brecciated. Among these, very high

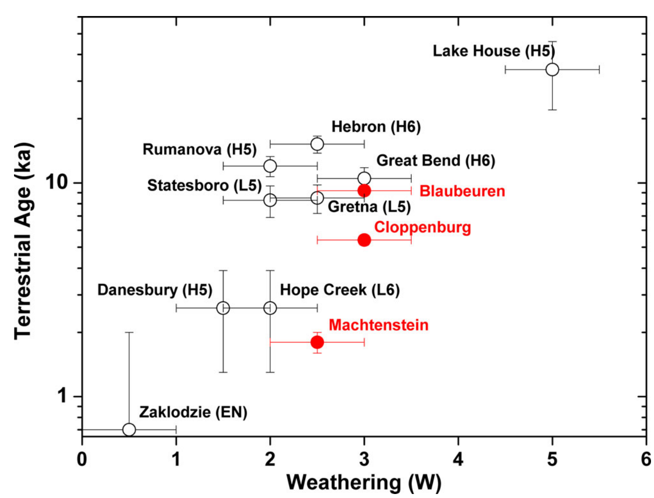

Fig. 9. Relationship between the degree of terrestrial alteration (Wlotzka, 1993) and the terrestrial age of chondrites found in areas with similar environments to that of Germany. The diagram includes data from the Meteoritical Bulletin, Rojkovic et al. (1997), Patzer et al. (2002), and Pillinger et al. (2011, 2014). The weathering degree of Statesboro (W2) is estimated according to pictures published in the Meteoritical Bulletin. For the degree of weathering, an error of ±0.5 is assumed. (Color figure can be viewed at wileyonlinelibrary.com.)

abundances of brecciated LL chondrites were registered for all petrologic types (71–90%). Many of the H and L chondrites with the fragments of low petrologic types (types 3 and 4) are often breccias and also have highly equilibrated clasts (e.g., H3-6 or L3-5, etc.; Bischoff, Schleiting, et al., 2018). Considering the petrologic type 4 chondrites (H[or L]4, H[or L]4–5 [like Blaubeuren and Cloppenburg], H[or L]4–6), 21% of the H chondrites and 33% of the L chondrites are brecciated. In H and L chondrites with petrologic type 5 (H[or L]5 [like Machtenstein], H[or L]5–6), about 17% and 22%, respectively, of the meteorites are brecciated. Although Blaubeuren, Cloppenburg, and Machtenstein are all brecciated (Fig. 6), the degree of brecciation considering the number of mineralogically and chemically different lithic clasts is low and not comparable to other ordinary chondrite breccias, like NWA 869, NWA 10214, Plainview, or Adzhi-Bogdo (e.g., Bischoff, 1993; Bischoff, Geiger, et al., 1993; Metzler et al., 2011; Rubin et al., 2005, 2017; Sokol et al., 2007; Terada & Bischoff, 2009). These numbers (of ~20% for brecciated H4 and H5 chondrites) are relatively low when comparing them with numbers for carbonaceous and Rumuruti chondrites; in carbonaceous chondrites, brecciation occurs regularly and unbrecciated carbonaceous chondrites are the rare exception: All known CI (e.g., Alfing et al., 2019; Endreß & Bischoff, 1993; Morlok et al., 2006) and many (probably all) CM chondrites are brecciated (e.g., Bischoff et al., 2006; Bischoff, Ebert, et al., 2017; Kerraouch et al., 2021; Lentfort et al., 2021; Lindgren et al., 2013; Metzler et al., 1992; Rubin et al., 2007), and some of these chondrites contain very exciting, sometimes very old clasts (e.g., Bischoff et al., 2021; Bischoff, Patzek, et al., 2018; Kerraouch et al., 2019, 2021; Zolensky et al., 2015, 2017). This is also the case for other carbonaceous chondrite groups (e.g., CH, CR, CV) and Rumuruti chondrites as well as for very unusual breccias, like Almahata Sitta and Kaidun (e.g., Bischoff, 2000; Bischoff et al., 1988, 2010, 2011; Bischoff, Palme, et al., 1993; Endreß et al., 1994; Fruland et al., 1978; Goodrich et al., 2014; Horstmann & Bischoff, 2014; Patzek et al., 2018; Zolensky & Ivanov, 2003; Zolensky et al., 1996).

CONCLUSIONS

Within the last 7 years, three rocks found in Germany (Blaubeuren, Cloppenburg, and Machtenstein) were identified as meteorites, increasing the number of German meteorite finds to 19. All three rocks are H-group chondrite breccias, and they are severely weathered and have lost abundant original metals and sulfides by terrestrial alteration. The degree of terrestrial weathering roughly fits to the sequence of their terrestrial ages (Blaubeuren > Cloppenburg > Machtenstein). Within Cloppenburg, the very rare hydrated iron phosphate mineral vivianite ($Fe^{2+}Fe^{2+}_2[PO_4]_2{\cdot}8H_2O$) is present, which indicates that the chondrite was weathered in a very wet environment.

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