

HEXACHLORO-1,3-BUTADIENE—A METEORITE ETCH AND DENSITY MEASURING MEDIUM¹

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ABSTRACT

A common organic solvent, hexachloro-1,3-butadiene, serves as an excellent etch for highlighting schreibersite in meteorites. It is well suited for differentiating between cohenite and schreibersite. It is also a good medium for specific gravity measurements *provided* that the sample is not subjected to prolonged exposure to the solvent.

INTRODUCTION

It is common practice to use distilled water for measuring densities of minerals and rocks. In a recent paper Cabri (1969) suggested that hexachloro-1,3-butadiene (HCBD) is a superior medium because it has a higher density than water and is chemically inert. Its low toxicity compared to other organic solvents adds to its attractiveness. We therefore decided to use HCBD for measuring the densities of meteorites. In accord with the procedure of Cabri, a practical grade of HCBD (J. T. Baker Chemical Company) was used. It was passed through a column of basic alumina to remove traces of hydrogen chloride that may have been present.

In the course of our density measurements with HCBD, we noticed that polished specimens acquired an etch. Schreibersite [(Fe, Ni)₃P] was unaffected, whereas the surface of both kamacite and taenite were chemically altered (Fig. 1). We therefore decided to investigate the suitability and characteristics of HCBD as an etching agent, and its value as a specific gravity medium.

In the study of iron and stony-iron meteorites, it is difficult to distinguish between some of the major phases. Nital or picral etches may be used to separate kamacite from taenite and plessite. It is far more difficult to distinguish between schreibersite and cohenite [(Fe, Ni)₃C]. A copper-plating technique may be used (Nininger, 1951), but it produces copper contamination in the meteorite. Freshly prepared boiling sodium picrate solution may also be used (Perry, 1944), but it is danger-

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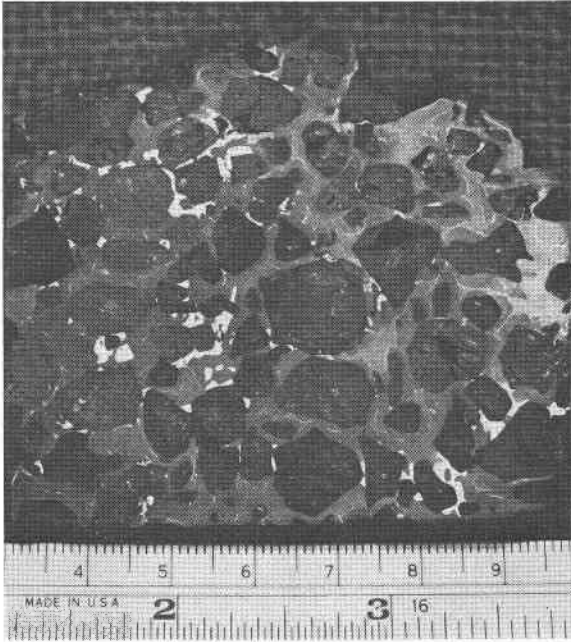


FIG. 1. *Ollague* pallasite etched by HCBD (experiment 1). White zones are unetched schreibersite. Dark angular grains are olivine. This photograph may be compared with Plate 1 of Buseck and Goldstein (1969)—the same meteorite, but not etched.

ous to handle; further, both of these techniques are uncertain in terms of their reliability. The HCBD, on the other hand, will etch cohenite while leaving schreibersite unaffected. Such an etch serves to highlight the distribution of these minerals within the metal phases much as a hydrofluoric acid etch followed by a sodium cobalt nitrite stain makes potassium feldspar stand out in polished slabs of granitic rocks (Nold and Erickson, 1967). Thus HCBD is very useful for purposes of estimating schreibersite and cohenite contents in meteorites by modal analyses. This information is needed to provide meaningful values of the total phosphorus and carbon concentrations.

EXPERIMENTAL DESCRIPTION AND RESULTS

The HCBD etch was initially discovered when a meteorite was immersed for one week. The extended time period was used in an effort to get an improved density measurement by displacing all of the air and water that may have resided in fractures. We wished to compare results obtained with a well-wetted specimen to those from a briefly immersed sample. A difference of roughly 0.5 percent in density was observed. More striking than this density difference was the pronounced etch that was produced (Table 1, experiment number 1).

Because of the expected chemical inertness of HCBd (Cabri, 1969) towards the meteoritic phases, the production of an etch was surprising. Experiments were designed to test the effects of several variables on the efficiency of etch production: (a) incident light, (b) surface contamination, (c) water and other impurities in the HCBd and (d) moisture in the air during the drying of the sample after immersion in HCBd. The results are discussed below, and are listed in Table 1.

Experiment 2 demonstrated the reproducibility of the etch obtained in experiment 1. The *Canon Diablo* iron meteorite was used in experiment 3 a-e to show that HCBd can be used to distinguish between cohenite and schreibersite.

An attempt was made to minimize the possible effects of surface impurities. In experiment 3e the sample was carefully cleaned by first scrubbing with detergent and distilled water, followed by washing with 95% ethanol, petroleum ether and finally with ethyl ether (AR). It was then immersed in HCBd. No marked difference was noted between this specimen and those which were not pre-cleaned, suggesting that surface impurities are not essential for the etch. To eliminate the possibility that the etch is produced simply by the action of moist air on metal, duplicate samples (8a and b) were exposed to H₂O-saturated air for twenty-four hours. Both samples were washed in distilled water and detergent (Alconox). One was then cleaned successively with 95% ethanol, heptane (Baker grade—purified), ethyl ether (AR), and acetone (AR). Although minor rust did develop along a few cracks, the mirror polish was not degraded on either specimen.

The possibility of a reaction in HCBd catalyzed by exposure to light was investigated by placing samples in a flask exposed to room light and duplicates in a flask in the dark (experiments 4 to 7). The extent of the etch was clearly and reproducibly greater in the samples that were exposed to the light.

We wished to eliminate the effects of impurities in practical grade HCBd. It was first passed over a weakly basic ion-exchange resin (Amberlite 1R-45) or stored over anhydrous potassium carbonate in order to remove strong acids such as hydrogen chloride. It was then distilled at atmospheric pressure. Only the center cut (bp 208.5° to 209°C) was used for experiments 4 through 7. To remove any free oxygen the distilled HCBd was degassed in the dark in the solid state (Dry Ice-isopropanol bath) under high vacuum. In the last stages the temperature was raised and the HCBd was allowed to melt while still under vacuum. The distilled, degassed HCBd was protected from air, water and light during succeeding experiments. Etches were obtained even with this purified material.

Degassed, distilled HCBd led to a significantly reduced rate of etch production on the immersed meteorites. One specimen (No. 4) showed no observable etch in the immersed state after a two week period; however, the same sample developed a pronounced etch in a few minutes when it was left to dry in the air after being removed from the HCBd. In contrast, etches produced in non-degassed and non-purified HCBd were visible while the specimens were still immersed (experiments 1 to 3). These results, therefore, suggest that the chemical processes leading to etching have a requirement for air and/or water vapor.

For those samples that were immersed in the degassed distilled HCBd, a drybox containing a helium atmosphere was used to isolate them from oxygen and water vapor. By also drying the specimens with helium after removal from HCBd we were able to control the effects of oxygen and water vapor. After drying in the helium atmosphere only a slight etch was observed. When the atmosphere in the drybox was changed to dry air, no change was produced on the specimens (experiments 5 to 7). However, when water-saturated air was introduced an etch developed. (This was independent of lighting conditions.) The etch did appear more pronounced, however, in specimens that had been exposed to a strong light source (experiments 4, 6a and 7a).

TABLE 1. DESCRIPTION OF EXPERIMENTS

Exp. no.	Meteorite name	Duration of immersion (days)	Grade of HCB D	Exposure to light	Atmosphere in flask	Drying procedure	Nature of final etch	
							Kamacite ^a	Cohénite
1. <i>Olague</i>		7	Practical	Room light	Air	Air	Brown	Np ^b
2. <i>Imitac</i>		7	Practical	Room light	Air	Air	Brown	NP
3. <i>Canyon Diablo</i>								
a)		7	Practical	Room light	Air	Air	Brown	Light bronze
b)		7	Practical	Room light	Air	Air	Brown	Light bronze
c)		7	Practical	Room light	Air	Air	Brown	Light bronze
d)		7	Practical	Room light	Air	Air	Brown	Light bronze
e)		3	Practical	Room light	Air	Air	Brown	Light bronze
4. Albin		14	Degassed Distilled	Room light	He	Air	Brown	NP
5. Spring water		19	Degassed Distilled	No	He	He→dry air →wet air	Reddish tan	NP
6. <i>Canyon Diablo</i>								
a)		8	Degassed Distilled	Room light	He	He→dry air →wet air	Reddish brown	Bronze
b)		8	Degassed Distilled	No	He	He→dry air →wet air	Reddish tan	Light bronze
7. <i>Canyon Diablo</i>								
a)		7	Degassed Distilled	100 watt bulb	He	He→dry air →wet air	Reddish brown	Bronze
b)		7	Degassed Distilled	No	He	He→dry air →wet air	Reddish tan	Light bronze
c)		0	—	Room light	Air	He→dry air →wet air	NC ^c	NC
8. a) <i>Canyon Diablo</i> (Routine cleansing)		1	—	Room light	H ₂ O-saturated	Air	NC	NC
b) <i>Canyon Diablo</i> (Thorough cleansing)		1	—	Room light	H ₂ O-saturated	Air	NC	NC

^a In all instances the taenite etch is similar, but less intense than kamacite; schreibersite is always unattacked.

^b No cohénite present.

^c No change observed.

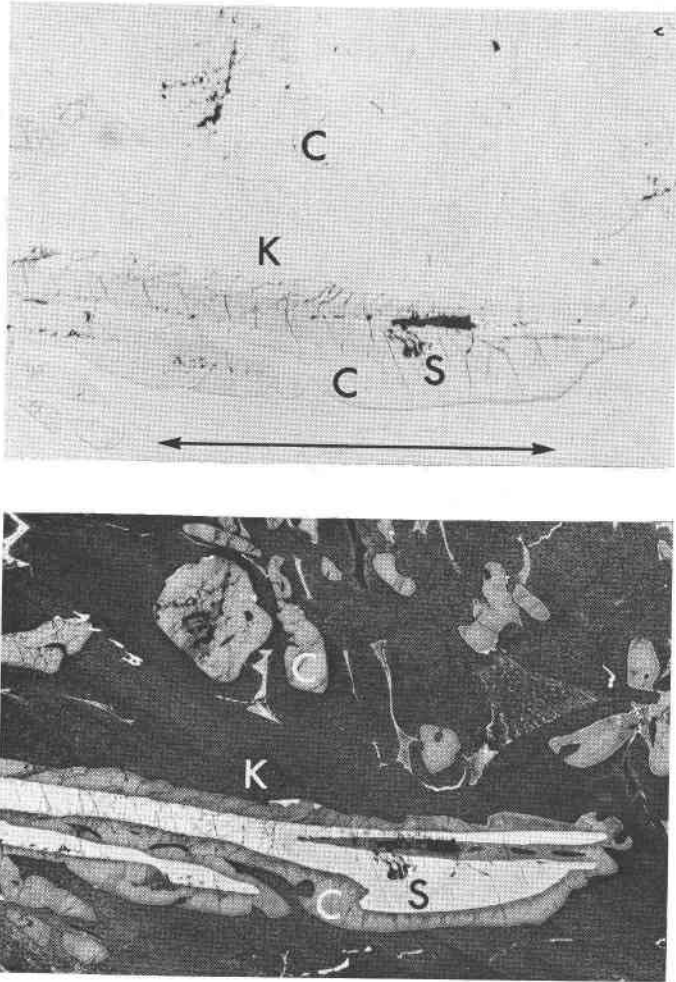


FIG. 2. *Canyon Diablo* octahedrite. Top—unetched specimen. Bottom—etched in practical grade HCBD for 24 hours. Note the contrast between schreibersite (S) and cohenite (C), both in the main masses and the small grains within the kamacite (K). Scale bar equals one centimeter.

DISCUSSION

The appearance of the metal etches varied considerably. Those specimens that were immersed in purified HCBD and then exposed to moist air had their polishes dulled, while developing a brownish, rustlike appearance. Under the microscope small reddish resinous globules are evident; they are most concentrated near grain boundaries and especially

along the fractures in cohenite. The practical grade of HCBd produces a more efficient dulling of the surface, resulting in a matte-like finish that has the appearance of being a deeper etch. In both cases kamacite shows greater evidence of reaction than does taenite. In none of the cases was schreibersite attacked.

In trying to define the chemical reactions involved in the etching process we note that the experimental observations are consistent with the development of a thin film of ferric chloride on the surface of the specimen. Moist air permits the formation of the red globules, presumably a hydrated ferric chloride. Further reaction with moist air then develops iron hydroxide, thereby producing the rust-like appearance. If the original film is ferric chloride, it may originate from the gradual development of traces of hydrogen chloride in the HCBd. It may be noted that Buddhue (1957) has observed that while schreibersite is resistant to acids, cohenite is not. This is consistent with the proposed origin of the etch.

Microchemical tests for chloride ion (Cl^-) were performed on the etched sample surfaces. A drop of distilled water was placed onto the sample surface to dissolve any inorganic chloride. To this was added 0.1 *M* silver nitrate. In control runs a white silver chloride precipitate developed at chloride concentrations of 0.0001 *M* or greater; however, no unambiguous precipitates were observed from the etched specimens. On the other hand, electron microprobe analysis comparisons between the etched and repolished surfaces showed a minor difference in chloride content; the etched portion developed a peak slightly over background. However, the difference is small enough to leave room for doubt as to whether there is a significant difference in chloride concentration.

CONCLUSIONS

HCBd serves as a good etching agent to distinguish between the opaque phases in iron and stony-iron meteorites. It is particularly well suited for differentiating schreibersite from cohenite. Schreibersite always retains its polish and original appearance while cohenite changes to a bronze color. The reflectivity of cohenite is diminished, although not nearly as markedly as is kamacite. The kamacite loses its polish and attains a flat brownish color. Taenite, plessite and sulfides also are dulled although generally not as greatly as kamacite.

In order to produce an etch the polished specimen must be thoroughly cleaned and then submerged in HCBd for a few days. Either purified or practical grade HCBd will work. If aerated practical grade HCBd is used, the immersion time is drastically reduced. To highlight schreibersite, as for point-counting phosphide, the etching should be done near a light source. When the specimen is removed from the HCBd it should

be rinsed immediately with alcohol and then wiped with a cotton-tipped swab soaked in alcohol or acetone. A second rinse may prove useful, after which the specimen should be dried. If a thick layer of globules forms, they may be removed prior to microscopic observation by again wiping the surface.

Our results do not disagree with the suggestion of Cabri that HCBd is a useful liquid for measuring densities. They do show, however, that care must be used to avoid reaction of the liquid with the material to be measured. Extended submersion should be avoided in order to minimize reaction, especially for reduced phases.

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REFERENCES

- BUDDHUE, J. D. (1957) The oxidation and weathering of meteorites. *Univ. N. Mex. Publ. Meteorit.* **3**, 161 p.
- BUSECK, P. R., AND J. I. GOLDSTEIN (1969) Olivine compositions and cooling rates of pallasitic meteorites. *Geol. Soc. Amer. Bull.* **80**, 2141-2158.
- CABRI, L. J. (1969) Density determinations: Accuracy and application to sphalerite stoichiometry. *Amer. Mineral.* **54**, 539-548.
- NININGER, H. H. (1951) Testing for cohenite and schreibersite. *Pop. Astron.* **59**, No. 5, 1-7.
- NOLD, J. L., AND K. P. ERICKSON (1967) Changes in K-feldspar staining methods and adaptations for field use. *Amer. Mineral.* **52**, 1575-1576.
- PERRY, S. H. (1944) The metallography of meteoric irons. *Bull. U. S. Nat. Mus.* **184**, 206 p.
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