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RECOVERY OF COESITE AND STISHOVITE FROM COCONINO SANDSTONE OF METEOR CRATER, ARIZONA[1]

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ABSTRACT

Coesite and stishovite, the high-pressure polymorphs of silica, can be recovered from shocked Coconino Sandstone by repeated treatments with hydrofluoric acid. Stishovite is not attacked by hot concentrated hydrofluoric acid and can be recovered quantitatively. Coesite is attacked by hydrofluoric acid but much less readily than is quartz. Treated at 25° C. repeatedly with a five per cent solution of hydrofluoric acid, most of the coesite is freed from the glass that was caused by the heat of impact of the meteorite. The coesite can then be separated from the residual quartz as colloidal and suspensoidal particles by repeatedly shaking in water in a one liter graduate and decanting. This procedure serves only as a means of recovery of coesite and is not a quantitative separation.

INTRODUCTION

Shocked Coconino Sandstone from Meteor Crater, Arizona, contains both coesite (Chao *et al.*, 1960), and stishovite (Chao *et al.*, 1962), the high-pressure polymorphs of silica. Many samples of this rock, ground to pass a 270-mesh sieve, were used in the work outlined in this paper.

It was found that stishovite was not attacked by either concentrated or dilute hydrofluoric acid. A sample of pure stishovite, the particle size of which ranged from 5 to 40 microns, and weighed two hundred milligrams, was treated on the steambath for four days with concentrated hydrofluoric acid in a covered platinum crucible. There was no measurable loss of weight. Therefore, the method for the recovery of stishovite given in this paper is a quantitative one.

Coesite is slowly attacked by hydrofluoric acid both at 25° C. and at steambath temperatures, but is more resistant to such attack than is quartz, as is shown in Table 1. The fused silica glass present in the Coconino Sandstone, that resulted from the heat of the impact of the meteorite, is readily destroyed by hydrofluoric acid, as is also the silica glass formed from the inversion of stishovite (Skinner and Fahey, 1963).

The procedure described for the recovery of coesite from shocked Coconino Sandstone is not a quantitative or even a semiquantitative one. It serves only as a means of obtaining pure coesite from the source rock, or when there is too little coesite present in the rock to give an *x*-ray powder pattern, to concentrate it so that the pattern can be obtained.

RECOVERY OF STISHOVITE

Stishovite is quantitatively determined by repeatedly treating the shocked rock with hydrochloric and hydrofluoric acids until only stishov-

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TABLE 1. TREATMENT AT 25° C. OF A 0.2000 G. OF COESITE (5 TO 40 MICRONS) AND 0.2000 G. OF QUARTZ (5 TO 50 MICRONS) WITH 100 ML OF A SOLUTION COMPOSED OF 95 ML OF H_2O AND 5 ML OF HF

Hours	Quartz	Coesite
0	0.2000 g	0.2000 g
1	0.1100	0.1615
2	0.0858	0.1568
3	0.0532	0.1477
6.	0.0274	
16	0.0231	0.0844
20	0.0078	0.0530
24	not measured	0.0275
48	not measured	0.0191
72	not measured	0.0114
96	not measured	0.0070

ite remains. The quartz and coesite present in the sample will be volatilized as silicon tetrafluoride. The feldspars, clays and other silicates, except zircon, that are usually present in trace quantities in Coconino Sandstone. are decomposed by the hydrofluoric acid and the cations present are converted to more or less soluble chlorides and fluorides and are removed by filtration.

The strength of the acids used, the ratio of the amount of hydrochloric to hydrofluoric acid, and the temperature and length of time of each treatment may be varied through wide limits in the quantitative determination of stishovite. The following procedure, monitored at intervals by *x*-ray powder patterns to show when pure stishovite has been obtained, is one of several that was found to be very satisfactory.

A 100 g. sample of shocked Coconino Sandstone (−270 mesh) was treated in a 1 liter platinum dish with 200 ml 1:1 HCl and 500 ml concentrated HF and taken to dryness on the steambath overnight. Next morning 50 ml of 1:1 HCl was added and taken to dryness on the steambath. Again 50 ml of 1:1 HCl was added and evaporated on the steambath until a volume of only about 10 ml remained. About 50 ml H_2O was added and the residual material was filtered on a 11 cm. Whatman No. 542 paper (a hard surface, and slow filter paper) and washed with 1% HCl solution. The residue was then transferred to a 100 ml beaker by means of a stream of water and dried on the steambath. The residue weighed 0.892 g, and the *x*-ray powder pattern showed it to be composed of about equal parts of stishovite and extraneous material.

The residue was transferred to a 100 ml platinum crucible and treated with a solution of 30 ml H_2O+30 ml HCl+30 ml HF. A well fitting cover was put on the crucible which was then allowed to remain on the steambath overnight. The residue was then filtered, washed and dried as outlined above. It weighed 0.569 g. The *x*-ray pattern indicated it to be predominantly stishovite with a minor quantity of extraneous material. Four more times the residue was treated as above with the H_2O, HCl and HF in the 100 ml platinum crucible and allowed to remain overnight, filtered, washed, dried, and weighed. Each time the amount of extraneous material was less than was present after the previous treatment until finally only a trace of zircon remained.

weight 0.892 g.	about 50% stishovite
weight 0.569	predominantly stishovite
weight 0.496	predominantly stishovite
weight 0.458	predominantly stishovite
weight 0.437	stishovite+trace zircon+trace(?)
weight 0.418	stishovite+trace of zircon

The 100 g sample taken contained 0.418 g. stishovite equivalent to 0.41% in the sample of Coconino Sandstone,+trace of zircon. Three or four faint lines of zircon were found in the *x*-ray powder photograph. A chemical analysis showed that there was 0.04% zircon in the stishovite.

Recovery of Coesite

Many samples of Coconino Sandstone were treated at both 25° C. and steambath temperatures with solutions of hydrofluoric acid and water that ranged from 1% to 100% by volume of hydrofluoric acid. The results indicated that a solution of 900 ml H_2O+50 ml HF at 25° C. was a satisfactory one for the treatment of 50 g of sample.

As outlined below the separation of a pure fraction of coesite required more than thirty days and was finally brought about by suspension in water after the coesite had been freed from the source rock by the weak solution of HF at 25° C.

The procedure is as follows:

Four 50 g. samples of shocked Coconino Sandstone (−270 mesh) were each placed in a 1 liter platinum dish and treated at 25° C. with 900 ml H_2O+50 ml HF and stirred well. One day later each was filtered on a 11 cm. Whatman No. 542 paper and without washing transferred back to the platinum dish and dried on the steambath. Each sample weighed 43 g. Again 900 ml H_2O+50 ml HF were added and the solutions stirred well each day for six days. As before the solutions were filtered, transferred back to the platinum dishes and dried overnight on the steambath. Each weighed 31 g. The process was repeated as above at 25° C. for six days and the weight of each of the four samples was reduced to 21.5 g.

The samples were combined to make two 43 g samples and the treatment was again repeated as above for 15 days. The two solutions were then combined and filtered, and then transferred to one of the platinum dishes and dried on the steambath; weight 59 g.

The residue of 59 g was then heated in a 100 ml platinum crucible in a muffle furnace between 900° C. and 1000° C. for $\frac{1}{2}$ hour to invert the stishovite present to silica glass (Skinner and Fahey 1963).

After cooling, the sample was transferred to the large platinum dish, and the treatment with 900 ml H_2O and 50 ml HF was twice repeated for six days. The weight of the residue was reduced to 49 g after the first of these two treatments, and 40 g after the last one.

At this stage, the coesite has been freed from the silica glass and further treatment by the dilute solution of hydrofluoric acid would slowly reduce the amount of coesite present.

The particle size of the coesite ranges from a maximum of about 40 microns down to colloidal size. Most of the coesite in the 40 g residue was separated by repeated shaking in water in a 1 liter graduate, allowing to settle and decanting. The first decanting of about 950 ml into a 1 liter beaker was made after 5 minutes of settling. The water was evaporated over night on the steambath and the residue weighed and x-rayed for purity.

About a liter of water was added to the residue in the graduate, which was then repeatedly shaken and decanted after settling for two hours. This was then repeated after settling for 5 hours and 6 times after a settling time of 24 hours each.

The fractions recovered after 5 minutes, 2 hours and 5 hours were discarded because there was more than a trace of quartz present. The six fractions each of 24-hour settling time contained only a trace of quartz as reported by the x-ray powder pattern. The weights of the six fractions were:

Fraction	Weight	
1st	1.15 g.	coesite
2nd	3.37	coesite
3rd	2.28	coesite
4th	0.95	coesite
5th	0.52	coesite
6th	0.26	coesite
Total	8.53	coesite

The next fraction contained more than a trace of quartz, so the separation was discontinued at this point.

The 200 g sample yielded 8.53 g of coesite that contained no zircon and only a trace of quartz. This puts a minimum of 4.26% coesite in the sample. The true figure is probably closer to 8%.

The minimum percentage of coesite that can be detected in a sample by the hydrofluoric acid treatment outlined above is probably not much less than 0.2%.

Coesite can be determined qualitatively in Coconino Sandstone by treating a finely ground 10 gm sample with 500 ml of 5% HF solution at 25°C for 24 hours, filtering without washing, and then drying the residue. An *x*-ray powder film will contain lines of coesite unless the percentage present in the sample is less than 0.2%.

The procedures outlined for stishovite and coesite apply very well when the source rock is shocked Coconino Sandstone. If the rock is one that contains feldspars, micas, and other silicates, there will be formed difficultly soluble fluorides and silico-fluorides. These can be removed by repeated treatments with boiling 1+1 HCl.

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