

bles. A thin coating of "Sauereisen" cement on the thermocouple junctions electrically insulates them from the sample holders.

The assembly, with one sample holder in place, is shown in Fig. 1. The other sample container, resting on top of the alundum block, is tilted to show the center thermocouple well. The center insulating tubing houses two thermocouples used to monitor the furnace temperature. They are connected to a recorder and temperature controller. The entire assembly, which may be exchanged for a conventional nickel block assembly, is supported by a collar which moves freely on a tubular stand (not shown). Exchange of the two types of sample holders is facilitated by quick-disconnect thermocouple lead connectors. By means of a clamp and locator-pin arrangement the samples are quickly and accurately positioned in the center of the furnace.

The quality of the DTA data obtained with the external thermocouple and platinum holders is illustrated by typical DTA curves shown in Fig. 2. The authors find the curves entirely satisfactory for most DTA purposes.

#### ACKNOWLEDGMENT

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#### SPONTANEOUS OXIDATION OF A SAMPLE OF POWDERED SIDERITE\*

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In checking over the analyzed samples left by the late Dr. Roger C. Wells, former geochemist, U. S. Geological Survey, it was noted that a powdered sample from near Linden, Texas, labeled siderite, had a marked reddish color, suggesting considerable oxidation of the ferrous

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iron. A determination of the ferrous iron content, made by J. J. Fahey in 1944, yielded the unexpected low result of only some six per cent FeO, a very considerable decrease from the original figure of 59 per cent determined by Wells in 1915. About 90 per cent of the original FeO content had spontaneously oxidized to  $\text{Fe}_2\text{O}_3$  within a period of 29 years. Since 1944 the oxidation has continued and now (May 1958) the percentage of FeO is less than one per cent. The color of the sample in May 1958 is very close to Ridgway's "Mahogany Red," Plate II, 7. R-O. k, and its smear is very similar to the adjoining "Burnt Sienna."

The occurrence of this siderite ore from the vicinity of Linden, Cass County, Texas, is given by Burchard (1916, p. 79-86). The analysis (Wells, 1937, p. 95-96) was made on an "average sample cleaned carbonate ore." As was customary in those days, the sample was powdered in a mechanically driven agate mortar, probably running for the better part of a day. Wells' analysis (FeO 59.42, MnO 0.13, CaO 0.16,  $\text{CO}_2$  36.54,  $\text{SiO}_2$  1.10,  $\text{Fe}_2\text{O}_3$  0.40,  $\text{Al}_2\text{O}_3$  1.02,  $\text{P}_2\text{O}_5$  0.11, S 0.05,  $\text{H}_2\text{O}^-$  0.15,  $\text{H}_2\text{O}^+$  1.05,  $\text{TiO}_2$  0.04, total 100.17) indicates an unusually pure siderite, the FeO content of the siderite being raised to 61.74 per cent (calculated percentage of FeO for  $\text{FeCO}_3$  being 62.01) after deducting nearly four per cent of impurities. These figures indicate that very little if any FeO was oxidized during the grinding.

The powdered sample was preserved in a glass tube closed with a cork stopper and lay in Wells' laboratory drawer undisturbed from 1915 to 1944 except for the transfer involved in moving into a new building in 1917. About 1950 the sample was transferred to a screw-top glass jar.

After Fahey's determination of FeO in 1944, no additional determination was made for a period of 10 years. In 1954, a determination of FeO gave a value less than half the amount found by Fahey, and it became evident that the ferrous iron content of the powdered sample was being spontaneously reduced as a function of time, and more frequent determinations were then run.

The results so far obtained, for decreasing percentages of FeO in a sample of powdered siderite as a function of time are as follows:

Date	Time in Years	Analyst	Percentage FeO
March 1915	—	R. C. Wells	59.42
May 1944	29	J. J. Fahey	6.23
May 1954	39	A. C. Vlisidis	2.38
May 1956	41	A. C. Vlisidis	1.70
June 1957	42	A. C. Vlisidis	1.20
May 1958	43	A. C. Vlisidis	0.74

In September 1955, Fred A. Hildebrand (U. S. Geological Survey, written communication) reported, on the basis of an  $x$ -ray pattern (film no. 8675), that the sample was “. . . hematite with small to moderate amounts of goethite and siderite and trace of quartz. The hematite appears to be poorly crystalline and has a unit cell somewhat larger than normal hematite.” The trace of quartz is 1.10 per cent of  $\text{SiO}_2$  by Wells' analysis.

Plotting the percentages of FeO shown above against time (years) and extending a straight line through the last five points, suggests that in early 1960, about 45 years after Wells' analysis, all the ferrous iron will have spontaneously oxidized to ferric iron.

These results lead to speculations on the history of natural deposits of ferric iron oxides. How many of these were at one time ferrous carbonates? These speculations we leave to the geologists. Burchard (1916, p. 76) noted the partial oxidation of nodular masses of siderite to iron oxide on Bowie Hill, Cass County, Texas, stating, “The iron carbonate is in general partly altered to limonite or to reddish hydrated oxides of iron, which form a scale or crust of varying thickness around the carbonate nucleus and along cracks which intersect the masses.” A massive sample of siderite perhaps could be protected from further oxidation by a surface layer of ferric oxide whereas no such crust of oxidized iron would form in a powdered sample.

What was it that caused the spontaneous, almost complete oxidation of this sample in approximately 43 years? Specimens of siderite in collections remain unoxidized for much longer time. Was there a latent after reaction due to the mechanical and thermal effects produced by, induced by, or accompanying the grinding of the sample?

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#### A QUANTITATIVE CORRECTION FOR THE HOLMES EFFECT

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The Holmes effect (1) arises in modal analysis because it is impossible to confine the observation to a single plane in a transparent specimen.