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# A NOTE ON THE EXAMINATION OF PYRITE IN CONVENTIONAL DIFFERENTIAL THERMAL ANALYSIS EQUIPMENT

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Examination of sulfide and arsenide minerals by the differential thermal method is now possible using the special equipment developed by Kopp and Kerr (1957), Dunne and Kerr (1960) and Pickering (1963), which prevents the corrosive sulfur and arsenic attacking thermocouple junctions and sample holders. However, these papers and that of McLaughlin (1957) do not fully illustrate the difficulties and the nature of the corrosion product that can be encountered when sulfide minerals occur in clay samples being examined in conventional DTA equipment, using nickel specimen holders. Some of these difficulties are discussed in the present note.

A clay sample containing 60% pyrite, 25% quartz, $<5\%$ kaolinite and traces of calcite, a montmorillonite mineral and goethite by *x*-ray examination gave the differential thermal curve A, Fig. 1. The equipment used was that described by Carthew and Cole (1953) with thermocouple arrangement as modified by Cole and Rowland (1961), and a nickel specimen holder. The low exothermic reactions in curve A, Fig. 1, if compared with that in curve C, Fig. 1 (in which the pen is off chart at 410° C. and from 625° to 825° C.) taken of the same sample in a stainless steel specimen holder, or if compared with the curve for pyrite described by McLaughlin (1957) give little evidence for the presence of any appreciable quantity of pyrite. In fact, the sharp endothermic reaction at about 670° C. suggests the presence of an amorphous or very reactive component not detected by the *x*-ray analysis. After the pyrite-rich clay had been run in the nickel specimen holder a small endothermic peak of unexplained origin was noticed as persistently occurring at 535° C. This is illustrated for a clay specimen in curve D, Fig. 1. It was established that this peak was reversible and was given when the specimen holder was empty of sample and/or inert material (calcined $Al_2O_3$). Clearly an endothermic reaction was being produced by a deposit on the differential thermocouple bead or on the walls of the specimen holder, caused by the decomposition of the pyrite in the earlier run. Since the differential thermocouple was of Pt/13%/Rh/Pt it was unlikely that the pyrite had reacted with it, and this was confirmed by clearing the bead with acid,

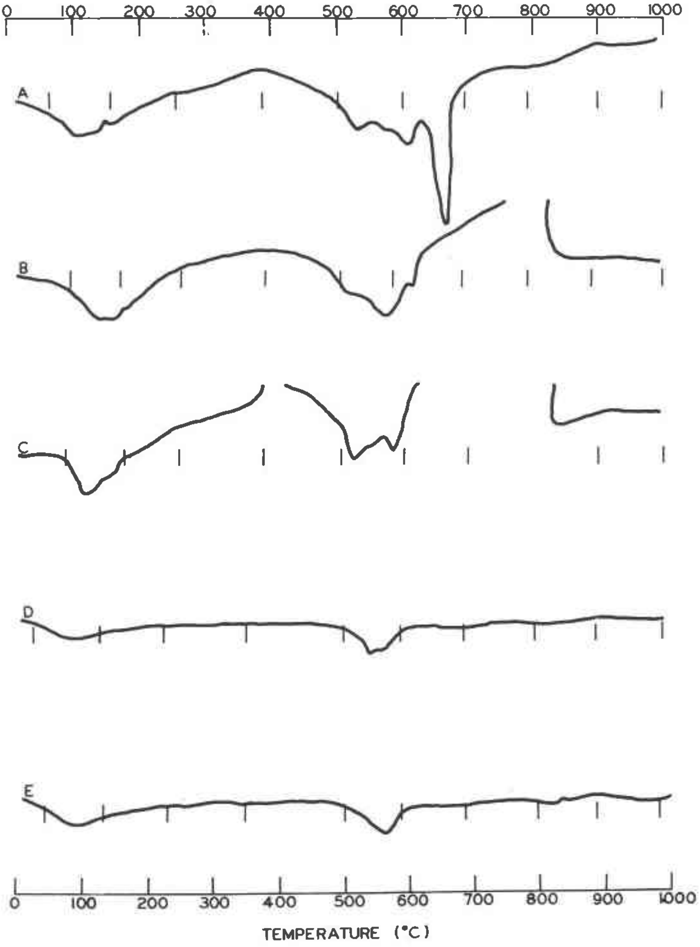

FIG. 1. Differential thermal curves of (A) pyrite rich clay run in a nickel specimen holder, (B) pyrite rich clay run in a clean nickel specimen holder, (C) pyrite rich clay run in a stainless steel specimen holder, (D) clay run in a nickel specimen holder subsequent to A, and (E) duplicate of D run in the cleaned nickel specimen holder.

filing it, and checking that the endotherm still persisted. Its origin obviously was to be associated with the specimen holder. A previous recognition by one of us (W.F.C.) that cracking in colored glass could be due to reversible low-temperature transitions in nickel sulfide minerals[1] led to the realization that a nickel sulfide mineral must have formed on the walls of the specimen holder through reaction between the nickel of the

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[1] Division of Building Research, C.S.I.R.O., Annual Report 1961–1962, p. 35.

holder and sulfur from the decomposition of the pyrite. *X*-ray examination of scrapings from the inside of the holder, using a Guinier-type focussing camera of 114.6 mm diameter with monochromatic copper radiation, proved the presence of $Ni_3S_2$ (heazlewoodite). Kullerud and Yund (1958/59) reported that $Ni_3S_2$ is readily synthesized in the dry way in silica tubes by mixing nickel with appropriate amounts of sulphur and heating the mixtures. They also show that at 550° C. ± 10° C. it goes through a high-low inversion. Heazlewoodite is the low temperature form; the high temperature form cannot be quenched. The small endotherm at about 535° C. is thus completely explained and was finally removed by re-drilling and thoroughly cleaning out the specimen hole in the nickel specimen holder (compare curves D and E, Fig. 1).

When the pyrite-rich clay sample was run in a stainless steel block, curve C, Fig. 1 resulted. This record is consistent with the high pyrite content of the sample for there is a large exothermic reaction commencing at 400° C. and finishing at 825° C., broken by apparent endothermic effects at 520°, 540° and 575° C. corresponding to periods when the mineral is in an inert atmosphere (McLaughlin, 1957). There is no sharp endothermic reaction at about 670° C. observed with the nickel specimen holder (curve A, Fig. 1). This endothermic effect is by no means reproducible. It was considerably less intense when the sample was run after the nickel sample holder had been cleaned but there was a following intense exothermic reaction (curve B, Fig. 1) not unlike that given by the sample in the stainless steel specimen holder and the holder was only slightly corroded. Kopp and Kerr (1958) consider it is probably due to the Curie point of $\gamma$-$Fe_2O_3$.

The differing differential thermal effects of a pyrite-rich clay sample run in a nickel and in a stainless steel specimen holder can probably be explained in the following manner. In a nickel specimen holder much of the sulfur formed from the dissociation of pyrite above 400° C. reacts with the nickel to form $Ni_3S_2$ instead of oxidizing to $SO_2$ with an intense low-temperature exotherm. The small amount of escaping $SO_2$ gas permits the early oxidation of the iron of the pyrite to $\gamma$-$Fe_2O_3$, which gives an endothermic Curie point at 670° C. followed by a low exothermic reaction from the transformation of $\gamma$-$Fe_2O_3$ to $\alpha$-$Fe_2O_3$. In a stainless steel specimen holder much of the sulfur formed from the dissociation of pyrite above 400° C. oxidizes to $SO_2$ with an intense low-temperature exotherm, and the escaping gas delays the oxidation of the iron of the pyrite to a temperature at which $\gamma$-$Fe_2O_3$ is unstable so that $\alpha$-$Fe_2O_3$ is formed directly with an intense exothermic reaction that terminates abruptly at 825° C.

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# BERYL IN A MONTANA TACTITE BODY[1]

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The contact-metamorphic zone at the Calvert Creek (Red Buttons) tungsten mine, in the SE$\frac{1}{4}$ sec. 12, T. 1 N., R. 13 W., Beaverhead County, Montana, (Walker, 1963, p. 4–7, fig. 2) has yielded one specimen of carbonate rock containing beryl in close association with epidote and small flakes of altered mica. Further search may discover a few additional specimens but probably not a sizeable deposit.

No detailed geologic work has been done in this region, which is underlain by both sedimentary and intrusive rocks. In the mine area, white crystalline limestone, probably a roof pendant of Meagher Formation (Cambrian), is in contact with quartz monzonite similar to that of the Boulder batholith. Strike and dip of beds differ greatly within short distances. Contact zones have been metamorphosed to irregular garnet-rich tactite bodies containing epidote, quartz, and a minor amount of chlorite.

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