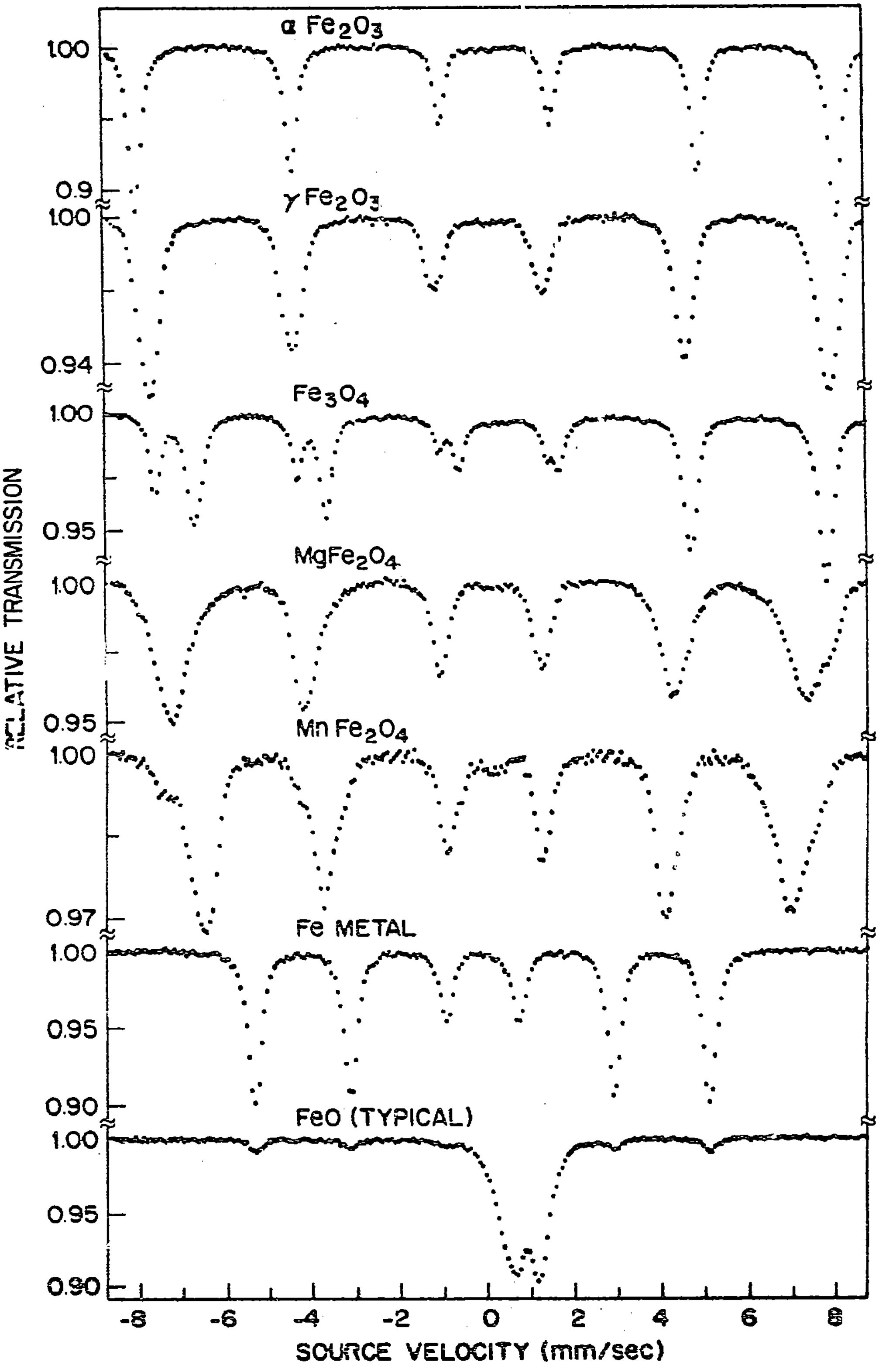

Fig. 1. Mössbauer spectra at room temperature of standards for comparison. (Note iron metal impurity in FeO.)

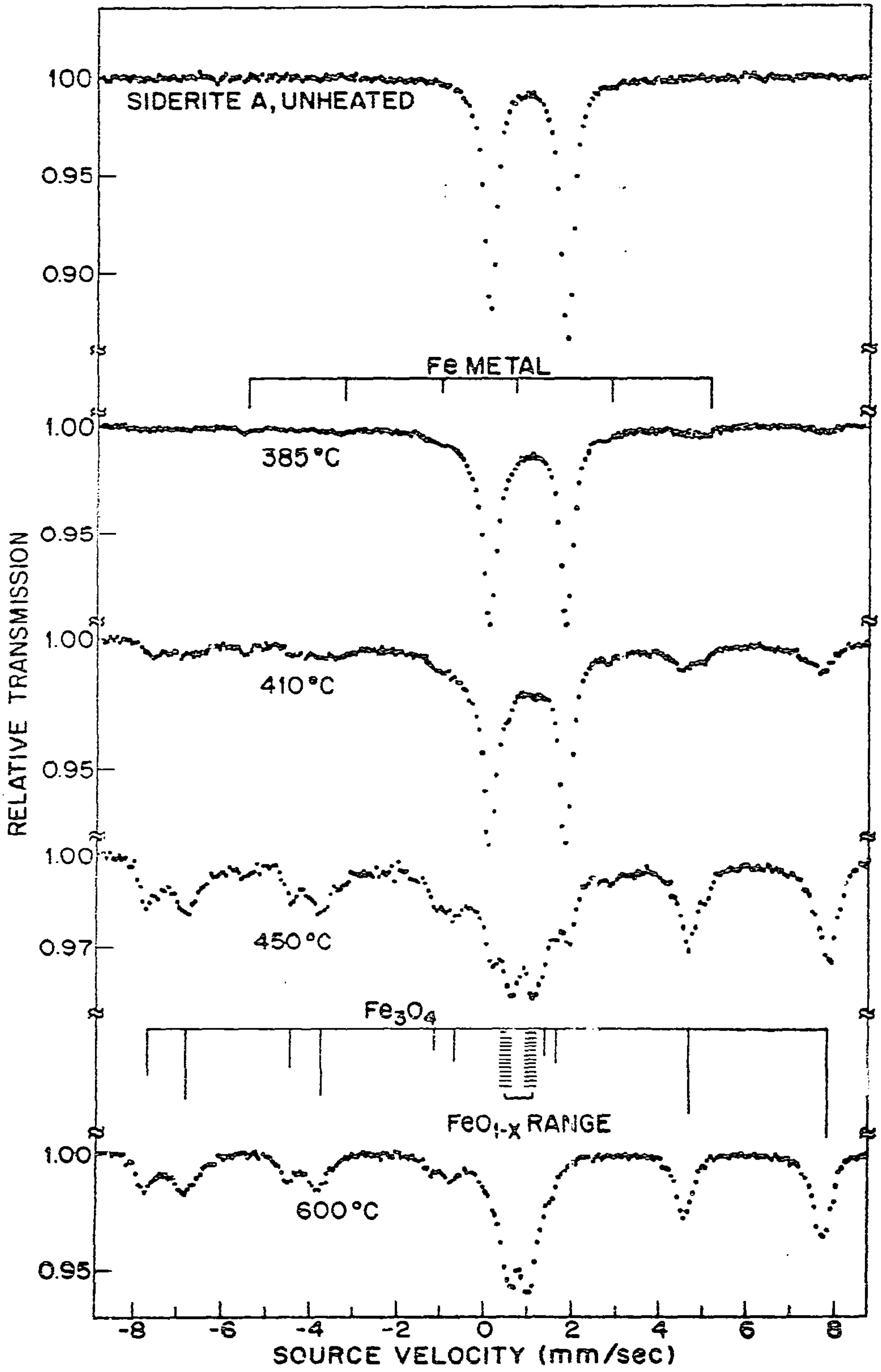

Fig. 2. Mössbauer spectra at room temperature of the products from relatively pure siderite at various stages during its thermal decomposition.

spectrum (IS = 0.85 ± 0.02 mm sec^{-1}, QS = 1.77 ± 0.03 mm sec^{-1}) agrees well with that reported by other investigators [7]. The early stages of the decomposition at 385 and 410°C show the introduction of iron metal and magnetite since it is well below the temperature for the disproportionation of wustite [eqn. (2)]. At the higher temperatures, 450 and 600°C, the decomposition of siderite is almost complete and the spectra of wustite and magnetite predominate. These conclusions are consistent with the earlier X-ray diffraction work [1] but the presence of iron metal is shown for the first time. Presumably the iron was either present in too small an amount or it was too finely divided or disordered to give an X-ray pattern as speculated earlier [1].

As can be seen from the standard curves in Fig. 1, the substitution of Mg or Mn for some of the iron leads to a reduction in the magnetic hyperfine splitting (MHS). There is a slight reduction in the MHS for the final product of the decomposition in Fig. 2 suggesting that some of the impurities were incorporated into the spinel phase. Earlier microprobe work in ferrites [3], however, showed that the bulk of the Mg will concentrate in the wustite phase. Since Mn is more capable of oxidation, some of it will distribute in the spinel and thereby reduce its MHS. An alternative conclusion, in the absence of the thermomagnetic data [1], would be that finely divided, i.e. superparamagnetic particles [8], were formed.

Results for the more impure siderite, B, are shown in Fig. 3. The Mössbauer parameters for siderite B at room temperature are IS = 0.84 ± 0.02 mm sec^{-1} and QS = 1.76 ± 0.02 mm sec^{-1}. Basically the same decomposition scheme has occurred. The main impurity now, however, is considerable Mg which leads to enhanced quadrupole splitting in the final wustite phase and a diminished B site component in the spinel phase. These changes are most evident in the final spectrum of Fig. 3. The quadrupole splitting in the wustite phase is also strongly dependent on both the degree of nonstoichiometry, i.e. excess oxygen or Fe^{3+} content, and the thermal history [9—11]. The latter affects how the cation vacancies are distributed or clustered. The spectrum of a sample heated to 600°C was virtually unchanged from that at 500°C. The reduced content of iron in the decomposition products of the impure siderite suggests that the large amount of Mg impurity probably stabilizes wustite with respect to disproportionation.

The complexity of Mössbauer spectra of wustite precludes extensive speculation. Greenwood and Howe [9—11] have shown that an observed spectrum is the sum of divalent components associated with several defect clusters as well as those having no defects, plus at least one component associated with the trivalent content. The situation is further complicated by the presence and distribution of significant amounts of impurities introduced in the naturally occurring minerals of this study.

Although a detailed analysis of the Mössbauer spectra associated with the decomposition of siderite is not attempted, it is nevertheless clear that the results are completely consistent with the conclusions of the earlier thermal analytical work [1,2]. At temperatures below 500°C the products of the thermal decomposition are iron metal and magnetite. Whether these are formed directly or via the disproportionation of a wustite intermediate

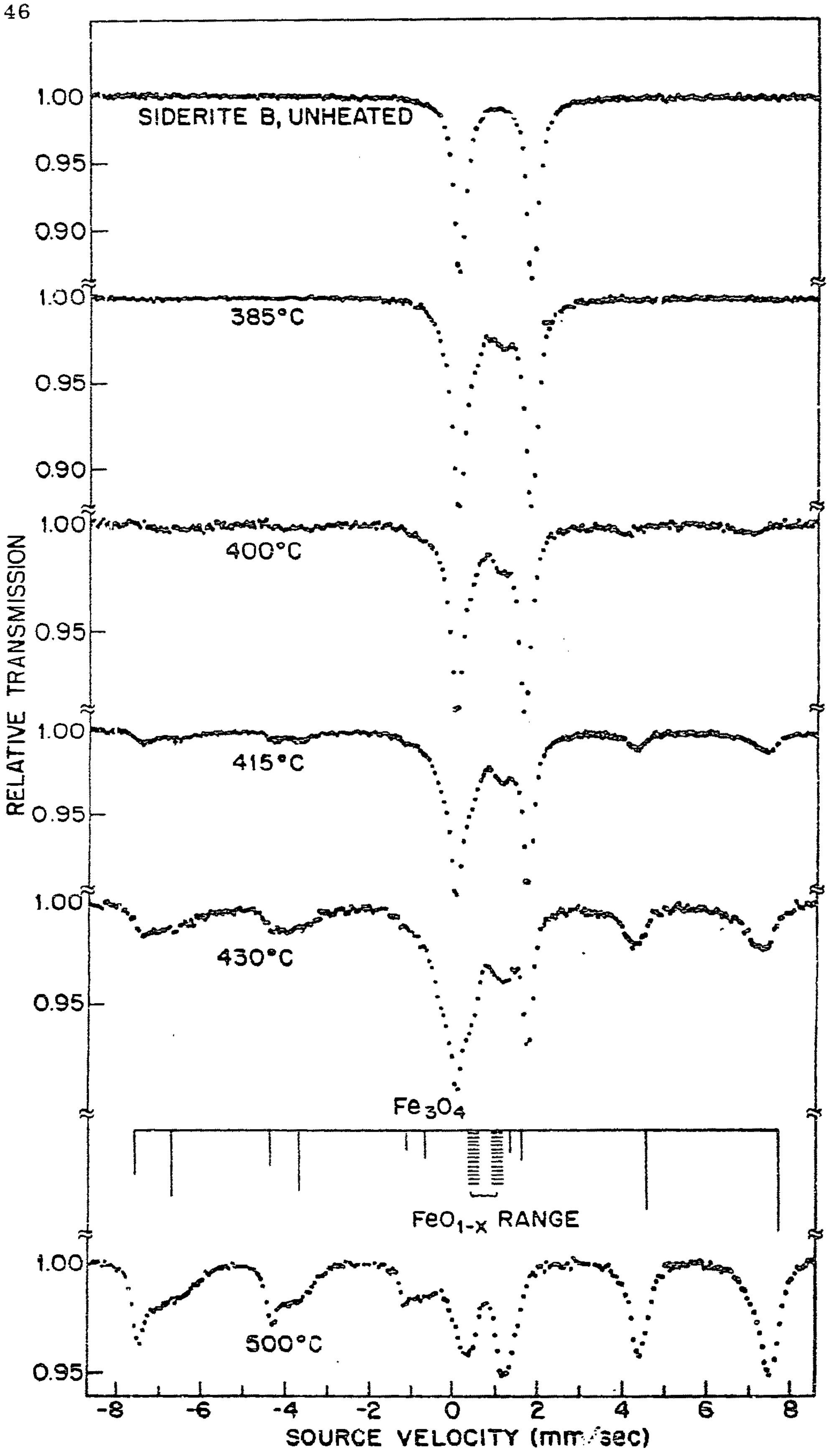

Fig. 3. Mössbauer spectra at room temperature of the products from a relatively impure siderite at various stages during its thermal decomposition.

cannot be established. The Mössbauer spectra reveal the presence of iron which could only be inferred earlier [1,2]. At higher temperatures, when the wustite is stable, it is the product along with an indeterminate amount of a magnetite (spinel) phase arising from oxidation by the carbon dioxide evolved during the decomposition. Divalent impurities tend to concentrate in the wustite phase and trivalent impurities in the spinel phase.

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