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The Inverse Peritectic Phase Transformation in the Fe-S System: Evidence for the Remelting of Troilite During Cooling

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In many nickel-iron meteorites, the troilite phase is characterized as shock melted, and it is typically found adjacent to annealed kamacite, which shows no signs of being shocked. This apparent variance in microstructural features between shocked troilite and annealed kamacite may be explained by an inverse peritectic transformation. This unusual transformation is well established within the Fe-S binary phase diagram, and in the analysis of weld microstructures.

The solidification and subsequent cooling of an alloy system containing Fe and S in excess of 0.01 weight percent (on a local scale) can be influenced by the inverse peritectic transformation. This reaction is defined as follows:

Solid1 → Solid2 + Liquid

In the Fe-S system, this transformation occurs at 1365C for sulfur contents between 0.065 and 0.14 weight percent. Assuming slow cooling through 1365C, the reaction is as follows:

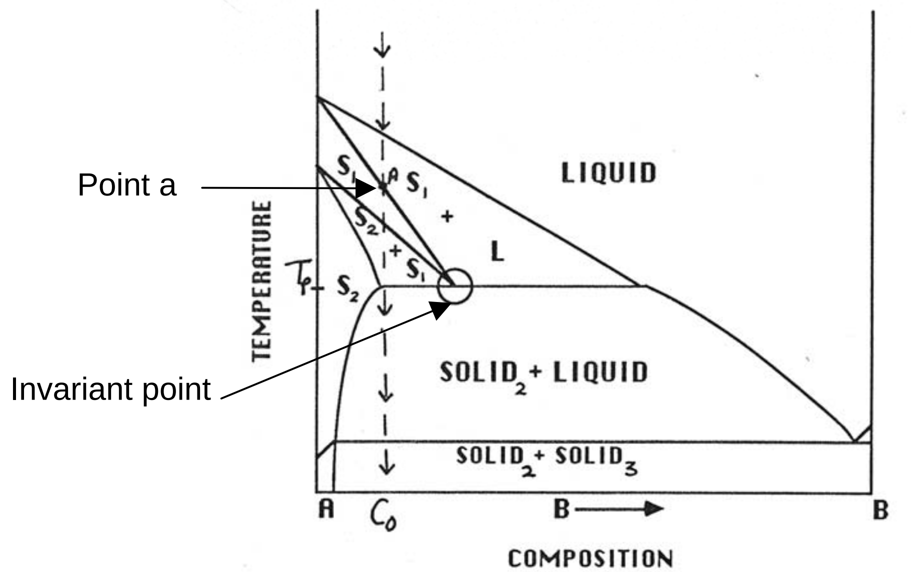
Body-centered cubic delta iron (kamacite) →

Face-centered cubic gamma iron (taenite) + Liquid (FeS).

Therefore, the single phase which was solid at higher temperatures now slightly remelts at a lower temperature. This new sulfur-rich liquid finally solidifies as the eutectic FeS or troilite at 988C.

Many nickel-iron meteorites share similar compositions with low alloy steels. If the bulk sulfur content is above 0.01 weight percent, such steels experience the inverse peritectic transformation during welding and subsequent cooling. Sulfur-enriched interdendritic areas are solid at high temperatures, but remelt on cooling, causing a loss of cohesion between dendrites. It is the commonality of composition between these low alloy steels and many nickel-iron meteorites which leads to a common response during cooling: the remelting of sulfur-enriched areas due to the inverse peritectic reaction.

A discussion of the role of the inverse peritectic transformation in troilite formation will be presented. Microstructural evidence of remelting in sulfur-enriched plessite areas, not previously considered in the literature of meteoritics, will be shown. It is postulated that the inverse peritectic transformation is responsible for the microstructural feature commonly characterized as "shock melted" troilite. This phenomenon of remelting during solid state cooling should be considered in the microstructrual analysis of extraterrestrial material containing iron and sulfur.



The inverse peritectic phase transformation: $SOLID_1$ <----> $SOLID_2$ + LIQUID

ON COOLING:

$SOLID_1$ ----> $SOLID_2$ + LIQUID

Fig. 1 The inverse peritectic phase transformation. The circled region highlights the invariant point associated with the transformation. In this discussion, consider only the reaction from left to right, the cooling of the system.

Consider the solidification of a material of nominal composition Co, represented by the arrowed line. The material is solid by Point a, entering a single phase region (S1). On further cooling, the material enters a 2-phase solid region (S1 + S2). Upon reaching the inverse peritectic temperature (Tp), the Solid 1 phase experiences the inverse peritectic phase transformation and dissociates into Liquid plus Solid2. The liquid persists until still lower temperatures, where the material solidifies completely for a second time at the eutectic temperature.

This type of transformation occurs in the Fe-S system.

Inset

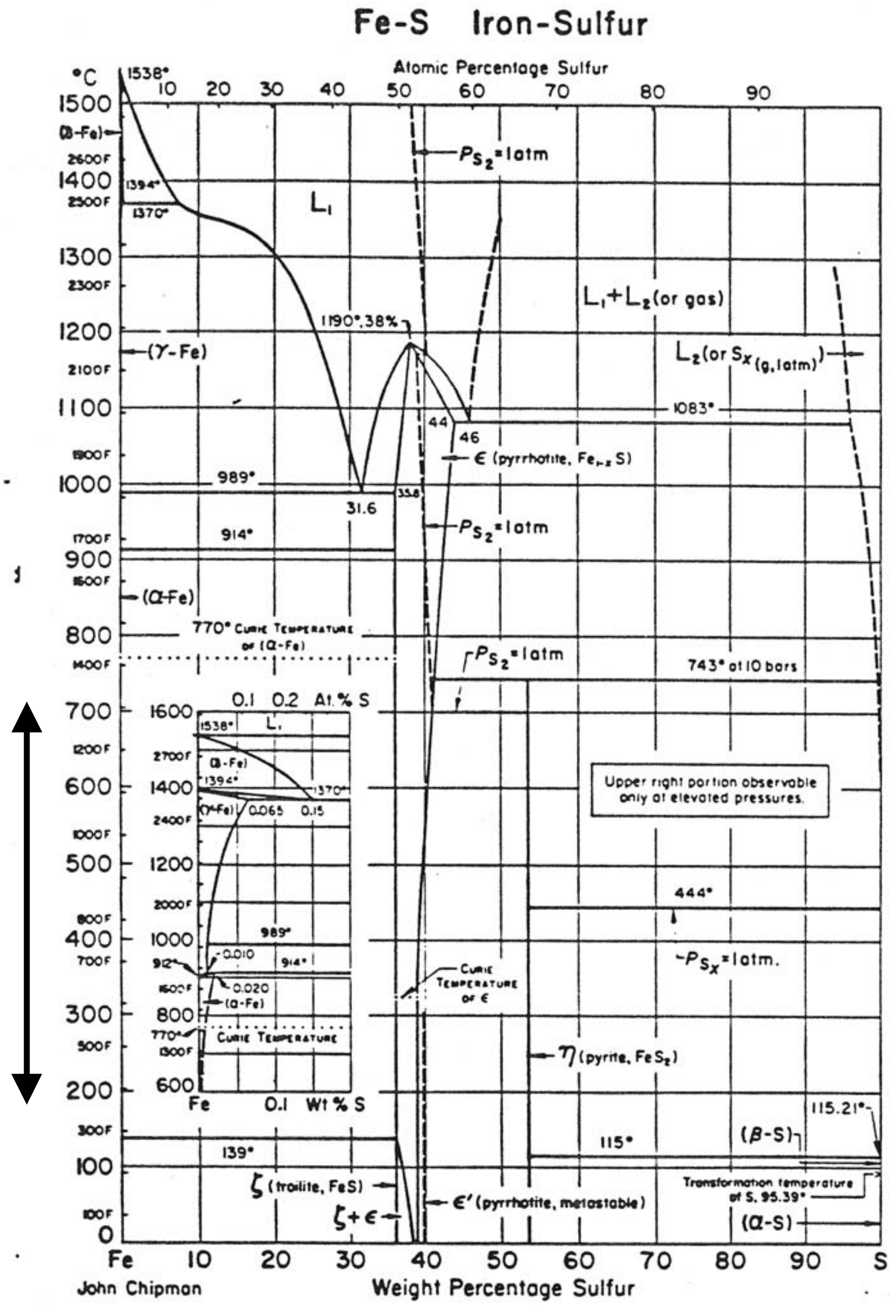


Fig. 2 The Fe-S phase diagram; American Society for Metals "Handbook." Inset is low sulfur region up to 0.2 w/0 sulfur, 600-1600C, containing inverse peritectic transformation.

Body-centered cubic delta iron (kamacite) → → →

Solid 1

Face-centered cubic gamma iron (taenite) + Liquid (FeS).

Solid 2

The boundary to keep in mind is the Liquid/Liquid + Solid which terminates in the eutectic at 988C, which appears very steep in this figure.

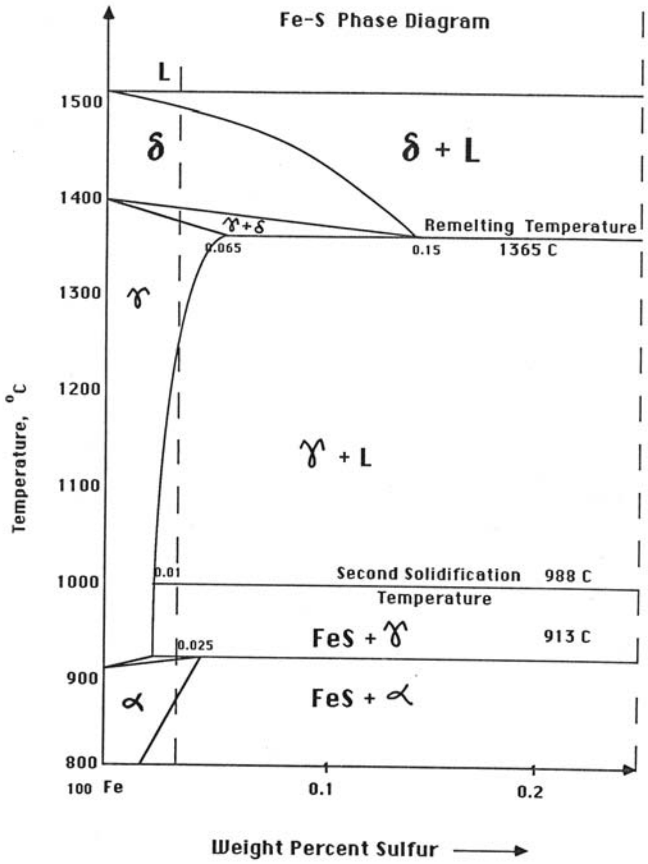


Fig. 3 Low sulfur region. It must be stressed that small amounts of trace elements can influence the position of phase boundaries. In a complex system like a meteoritic material, the exact position of these boundaries cannot be determined. Materials with local compositions between about 0.01 and 0.15 weight percent sulfur will experience the consequences of the inverse peritectic transformation on cooling. Material that is solid remelts at 1365C – or below – and solidifies for a second time at about 988C, the eutectic temperature.

For example, consider the equilibrium solidification of a material containing roughly between 0.01 and slightly less than 0.065 weight percent sulfur. Coming down the cooling path (dashed line), at ~ 1475C, the material passes through a single solid phase field, continues to cool, enters a two phase solid region briefly, passes through a single phase solid region and, at about 1250C again enters a two phase region in which one phase is a liquid. This material solidifies for a second time at the eutectic temperature, 988C.

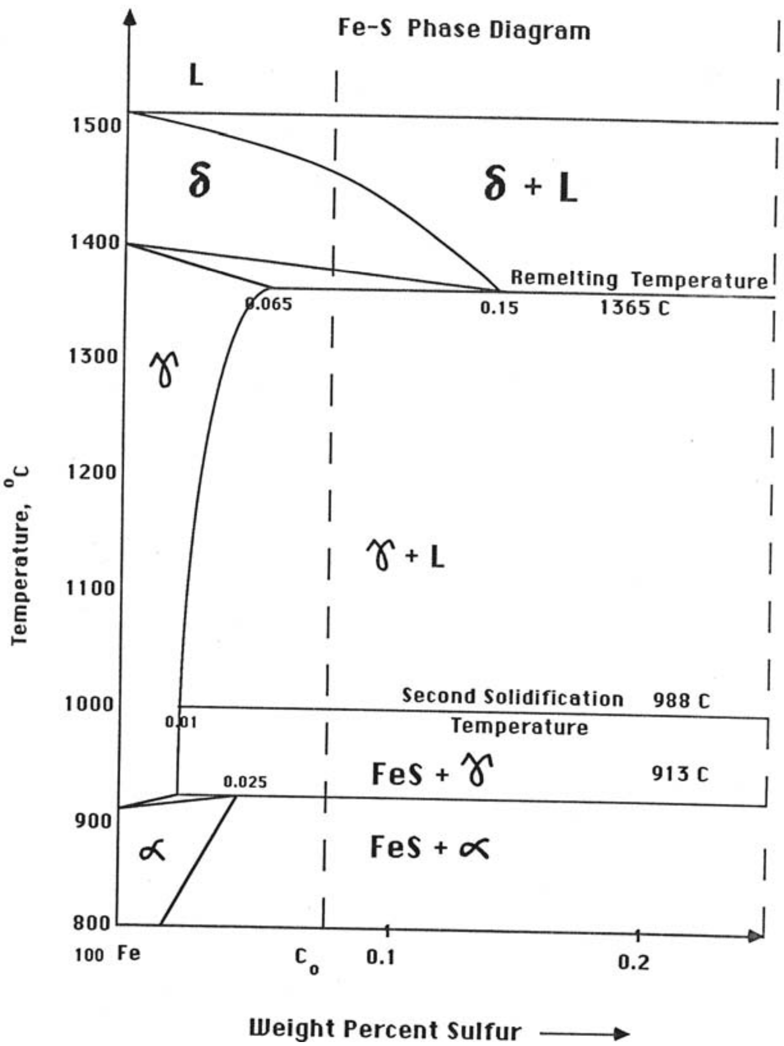


Fig. 4 Next, consider the equilibrium solidification (along the dashed line) of a material of nominal composition between 0.065 weight percent sulfur, the maximum solubility of sulfur in gamma iron, and 0.15 weight percent sulfur, the invariant point. This material, roughly 0.1 weight percent sulfur, is solid at about 1450C, goes through a single solid phase field (delta), then briefly into a two solid phase field (delta + gamma). At the inverse peritectic temperature 1365C, the delta phase experiences the inverse peritectic phase transformation by dissociating into gamma and liquid. The inverse peritectic transformation is the reason liquid appears at lower temperatures than expected. The material solidifies for a second time at the eutectic temperature, 988C.

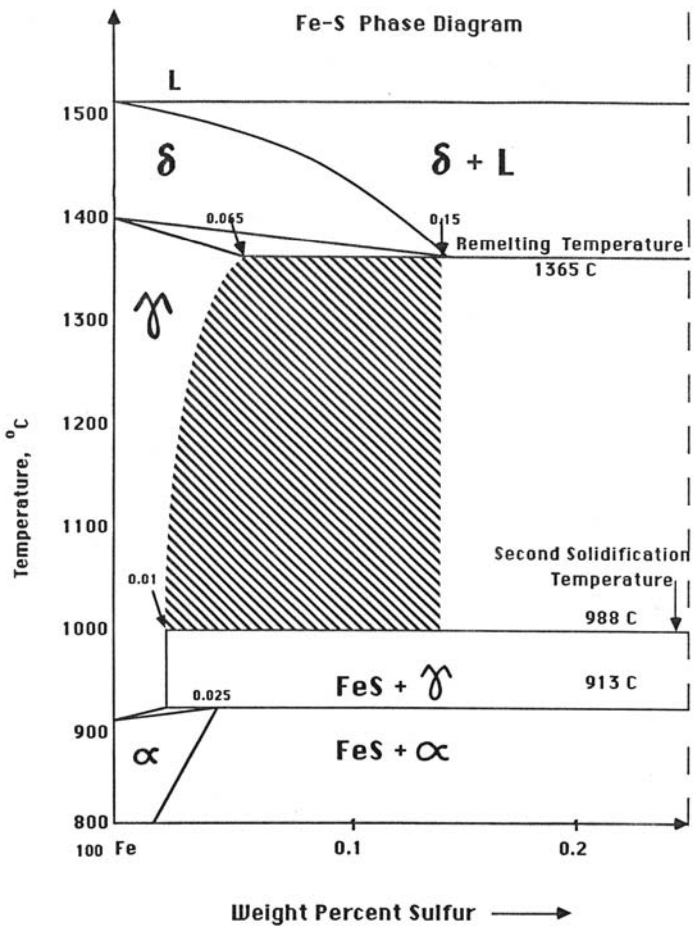


Fig. 5 Hatched area shows the range of temperature and composition over which liquid can occur for a second time, due to the inverse peritectic phase transformation. Liquid can reappear over a temperature range of 400C and over an order of magnitude in sulfur composition.

Springwater pallasite – stony iron

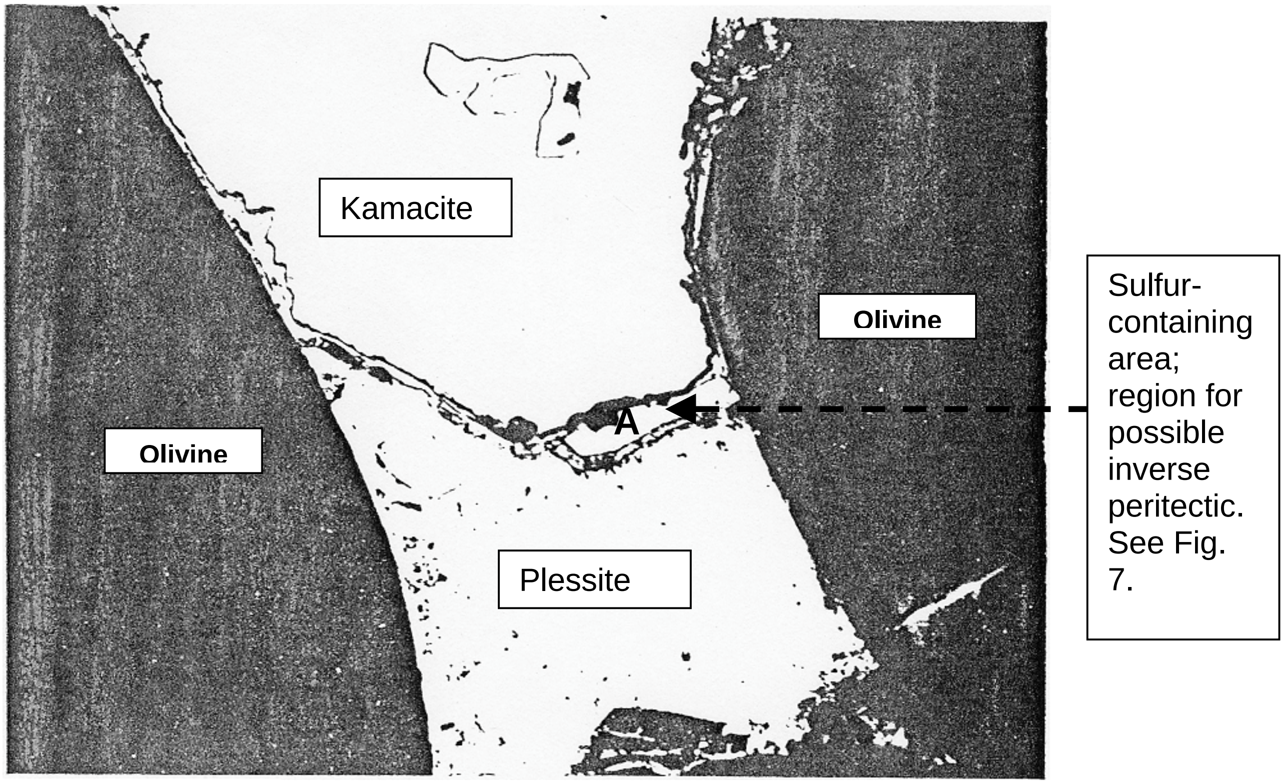


Figure 6 Area of Springwater pallasite (stony iron meteorite) subjected to EDAX analysis (50 x). See Fig. 7 for x-ray analysis of region A.

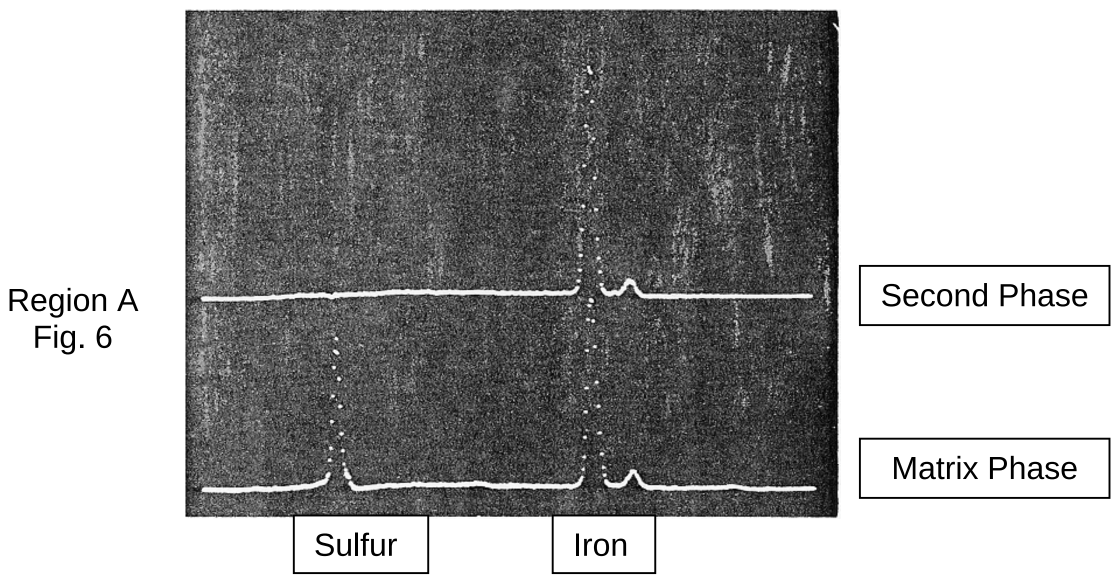


Fig. 7 X-ray emission spectrum of Region A (Fig. 6), Springwater pallasite. This EDAX scan shows the presence of iron and sulfur in the matrix phase, with iron the major component of the second phase. The area, in general, appears to be among the last to solidify and could be the product of eutectic liquid turning to eutectic solid during the inverse peritectic transformation.