CARBON AND SULPHUR IN THE CORE: AN EXPERIMENTAL STUDY

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INTRODUCTION

It is certain that planetary differentiation involves extensive melting of planetary materials through the decay of the short-lived radionuclides ^{26}Al and ^{60}Fe, and impact heating. Evidence from cosmochemical observations, refined seismic data, high-pressure experimentation, and theories of geomagnetism leads to the idea of iron being the dominant component of the cores of the Earth and other planetary bodies. Detailed comparison between the experimentally measured density of pure iron and the observed density of the Earth's core from seismic data revealed the density deficit in the core (both liquid outer core and solid inner core). The density deficit may be explained by incorporation of certain amounts of light elements (lighter than iron) such as sulfur (S), carbon (C), silicon (Si), and oxygen (O). During the core formation, it is likely that different amounts of light elements enters the iron dominant core depended on the initial composition and physical conditions of the core-forming event, such as pressure, temperature, oxygen fugacity. The composition and evolution of the core during cooling are strictly controlled by the melting relations and element partition in this multi-component system. Therefore, it is critical to understand melting behavior of Fe alloying with light elements at high pressure and temperature.

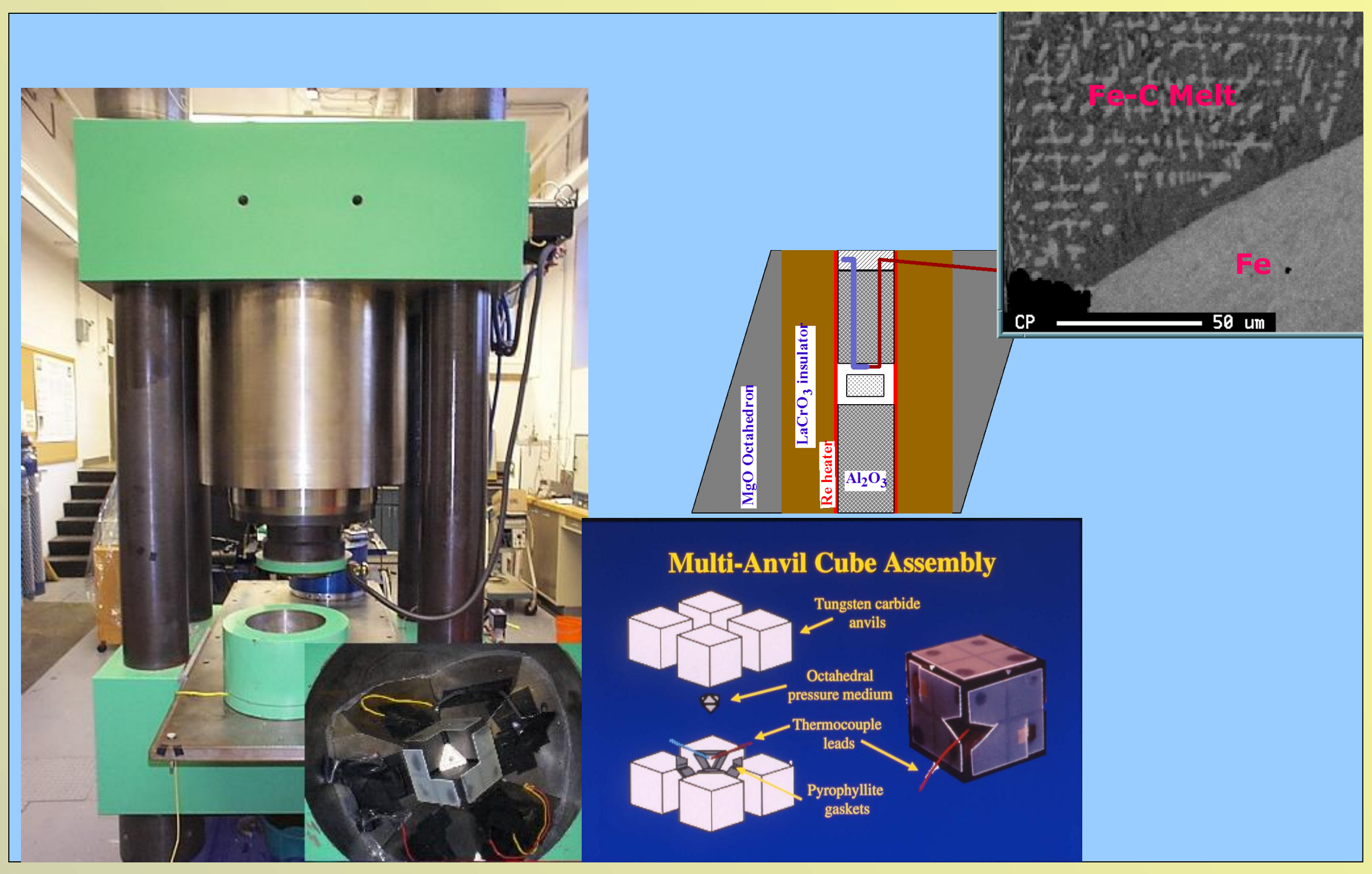


Fig. 1. A 1500-ton hydraulic press was used to generate pressure through a multi-anvil cell assembly that consists of eight truncated tungsten carbide anvils and a MgO octahedron sample assembly with a rhenium or graphite heater and $LaCrO_3$ insulator. Melting texture is shown in polished recovered sample.

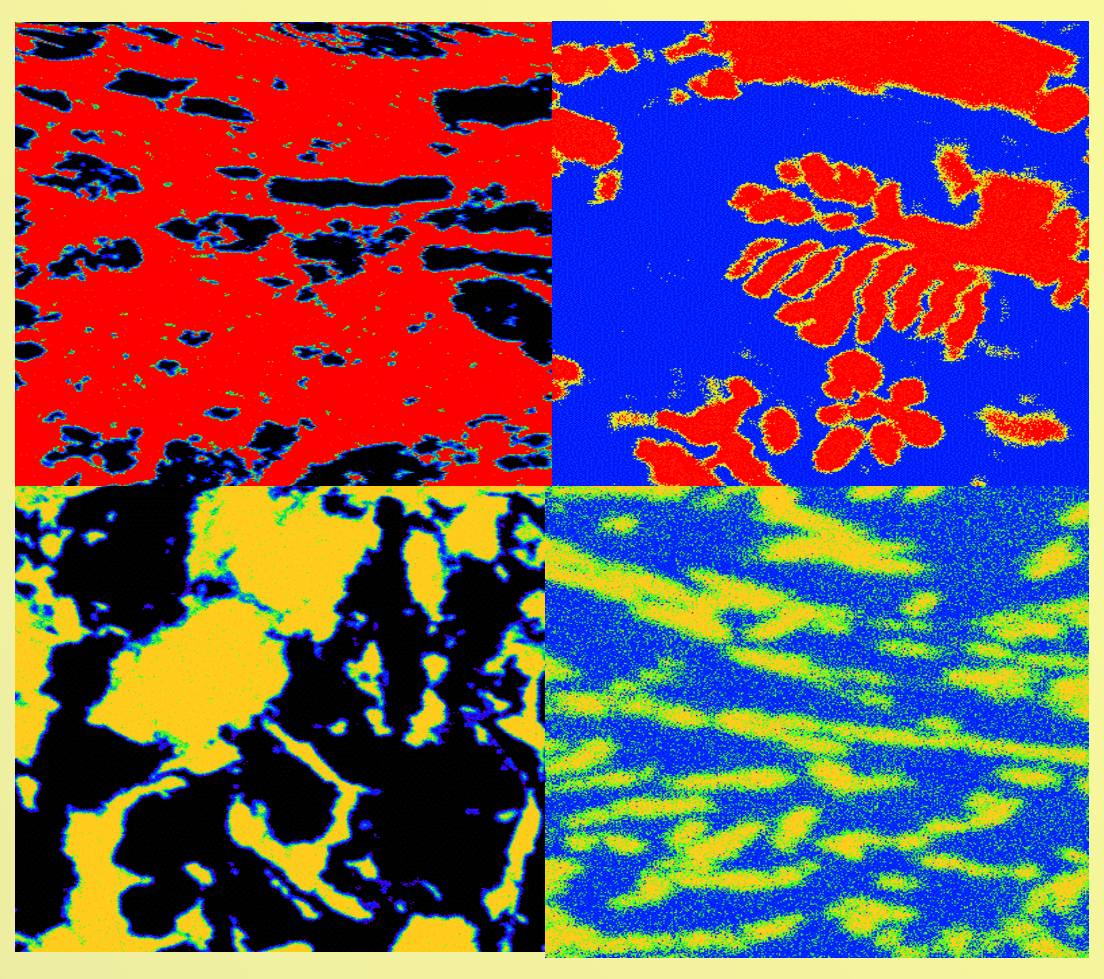
EXPERIMETAL PROCEDURE

Melting experiments in the systems Fe-S, Fe-C, and Fe-C-S were performed up to 25 GPa and 1973 K, using piston-cylinder and multi-anvil apparatus. Starting materials with different carbon and sulfur contents were prepared by mixing fine powder of pure iron (Fe), iron sulfide (FeS), and graphite (C). MgO capsules were used to contain the samples. For the multi-anvil experiments, well-calibrated high-pressure assemblies (18/11, 10/5, 8/3) were used to achieve high pressures up to 25 GPa. After reached the experiment pressures, samples were heated to the targeted temperatures, measured with W5%Re-W26%Re thermocouple. Samples were quenched to ambient condition and prepared for composition and texture analysis. Melting relations were determined with a JEOL JXA-8900 electron microprobe and SEM, based on quench textures and chemical composition analyses of the quenched phases. Powder X-ray diffraction technique was also used to identify phases and determine unit cell parameters.

The Fe-S System

Fe-S melt was the first melt to percolate through the surrounding silicates during differentiation because of the low eutectic melting temperature of the Fe-FeS system. We have systematically determined the change of melting relations and the eutectic temperature as a function of pressure in the Fe-FeS system (Fig. 2). The eutectic temperature in the Fe-FeS system initially decreases with increasing pressure, and then increases at pressures above 14 GPa after new high-pressure iron-sulfur compounds (Fe_3S_2, Fe_2S, and Fe_3S) forms. While the eutectic temperatures are taken as the minimum required for a partially molten Martian core, the liquidus temperature for the model core composition defines the minimum temperature required for a completely molten liquid core. We have further determined the liquidus temperatures in the iron-rich region, using multiple sample chambers techniques (Fig. 3). The melting relations at 21 GPa are shown in Figure 4.

The high-pressure experimental melting data provide important constraints on the physical state of the Martian core. The eutectic temperatures in the Fe-Ni-S system at core pressures are so low (~1400 K) that any amount of S in the core would lead to at least a liquid outer core for any reasonable thermal models. Given an estimate of present-day core temperature of 2000 K and a model core composition containing14.2 wt% S, the Martian core is most certainly liquid (Fig. 5).



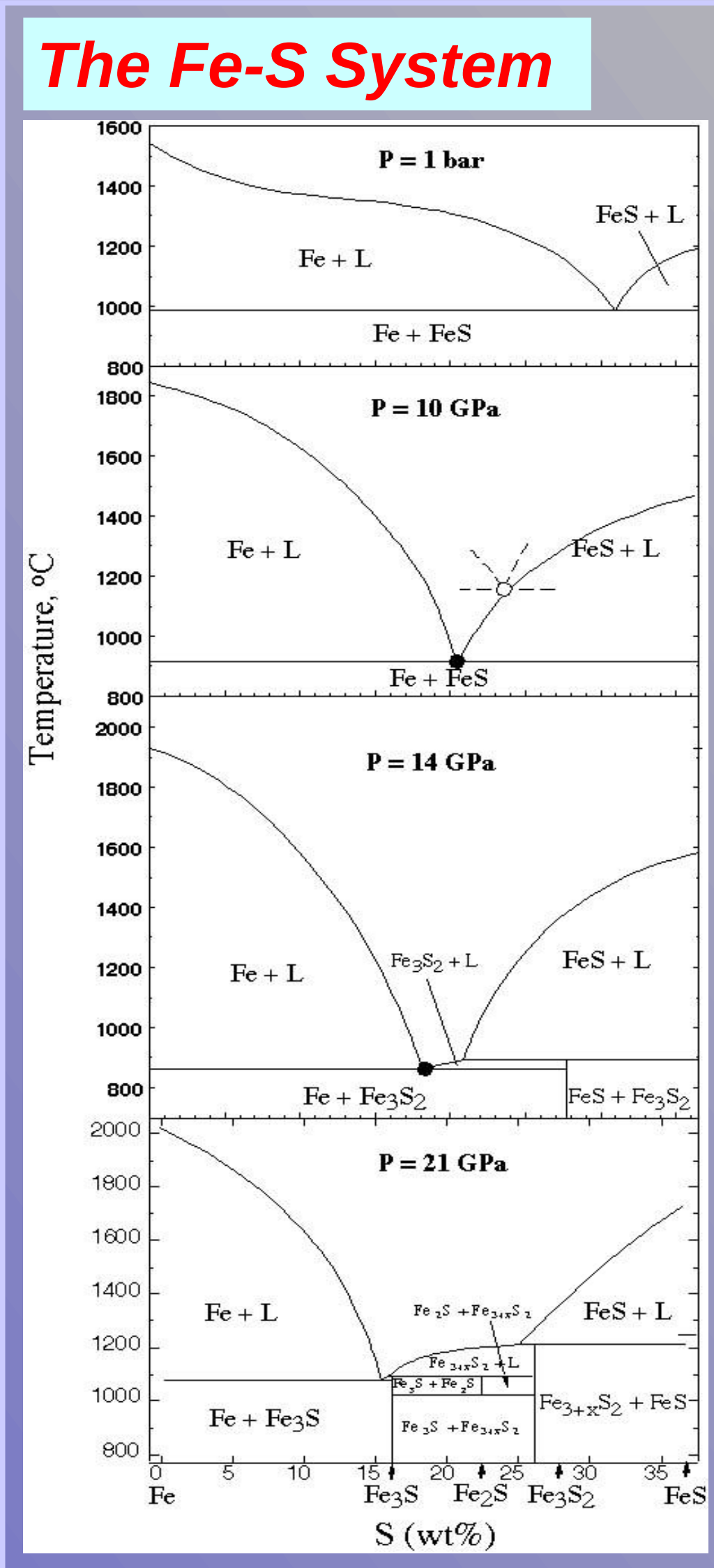


Fig. 2. Melting relations as a function of pressure in the Fe-FeS system.

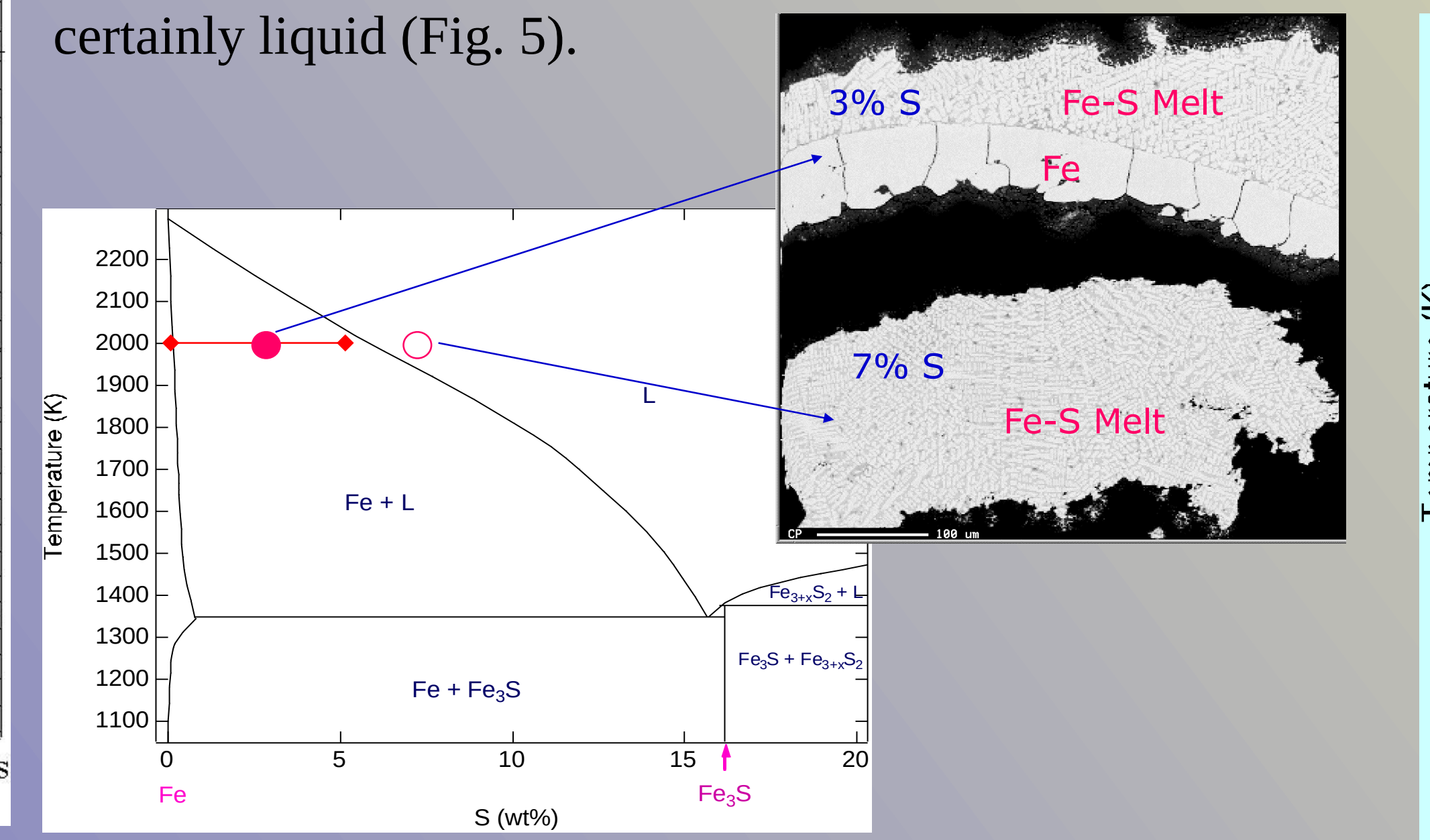


Fig. 3. The sulfur partitioning between solid iron and liquid was precisely determined using the multiple sample chambers technique.

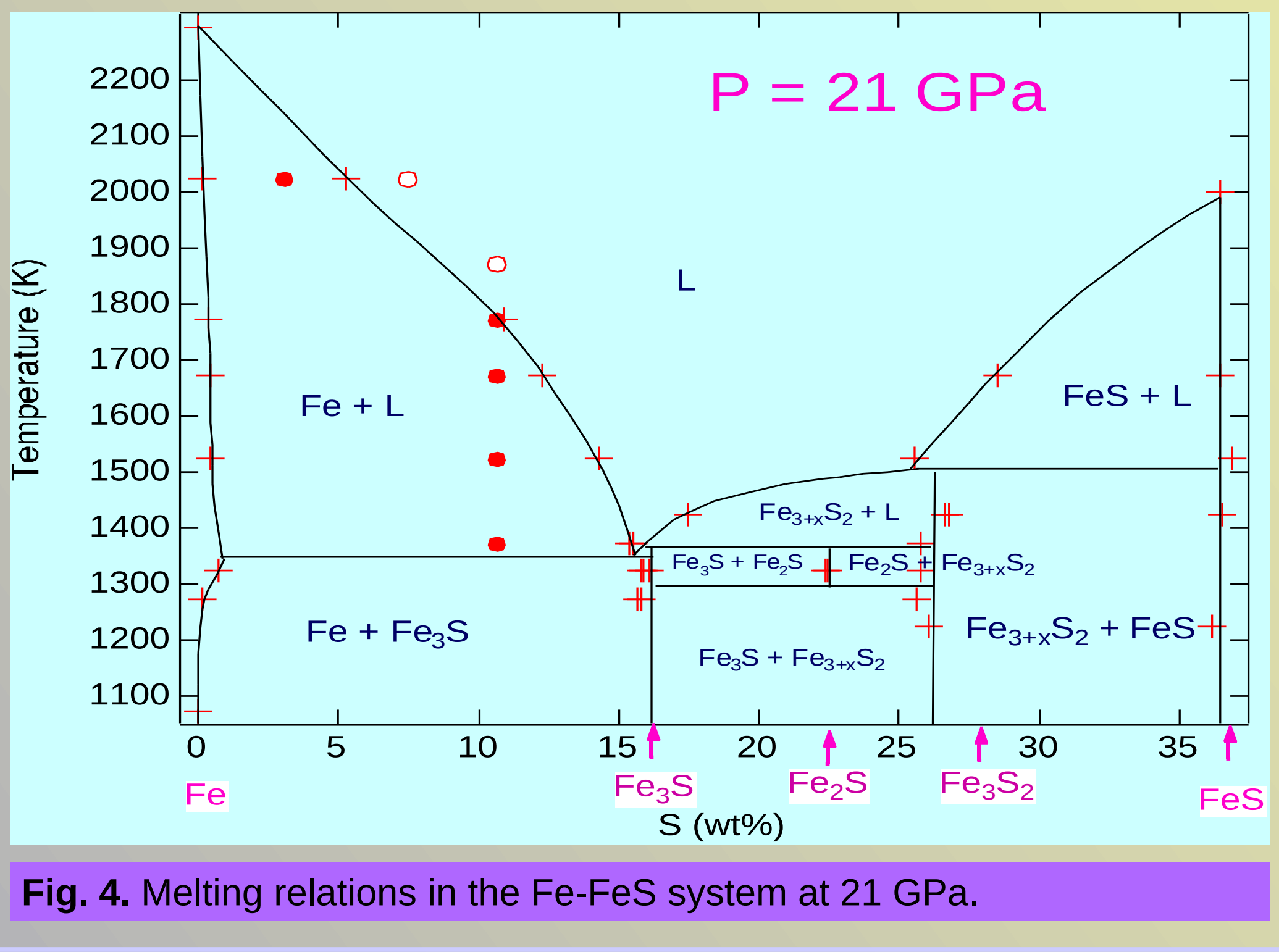


Fig. 4. Melting relations in the Fe-FeS system at 21 GPa.

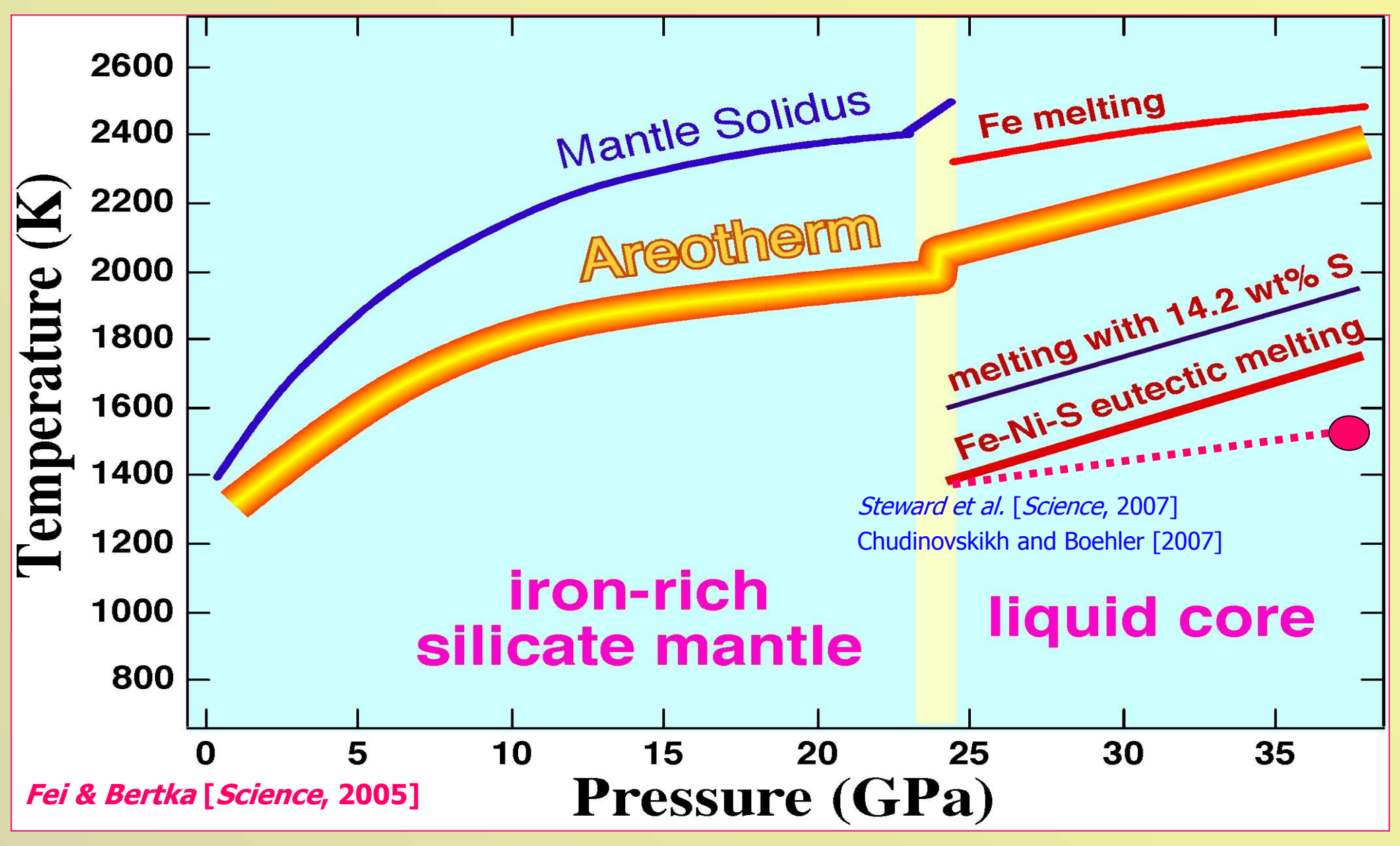


Fig. 5. Melting curves of Martian mantle and core materials compare with the estimated temperatures of the Martian interior.

The Fe-C System

Carbon (C) is another important light element to be considered. Carbon is relatively abundant in the solar system (e.g., 12xSi) and carbonaceous chondrites contains an average of ~3.2 wt% C. However, the estimate of the total C budget in the Earth is highly uncertain, ranging from 0.07 to 1.5 wt%, because of its high volatility. Furthermore, the C content in the mantle and the C partition coefficient between silicate mantle and metallic core are not well constrained. Therefore, it is impossible to provide tight constraints on the C content in the core from cosmochemical argument. On the other hand, it is well established that there are about 6-10% and 2% density deficits of the outer core and inner core, respectively, comparing to the density of pure iron, on the basis of geophysical observations. If C is responsible for part of the density deficit in the core, we can provide quantitative estimate of the C content in the core, providing the phase relations in the Fe-C system and the effect of C on the physical properties of Fe-C alloy are known. The focus of this research is to determine the melting relations in the Fe-C system and C solubility in metallic iron at high pressure. The project is aimed to understanding carbon distribution between inner and outer cores, the form of carbon incorporated in the inner core (dissolved carbon or iron carbide), and the percentage of C required to explain the density deficits.

We have carried out extensive experiments at 5, 10, 20, and 25 GPa to determine the melting relations in the Fe-C system as a function of pressure (Figs. 6 and 7). The eutectic temperature increases linearly with increasing pressure (Fig. 8). Our study presents directly experimental measurements of the melting relations in the Fe-C system at high pressure and temperature, which can be used to evaluate the incorporation of carbon into the planetary cores and its distribution between the inner and the outer cores if the core solidifies.

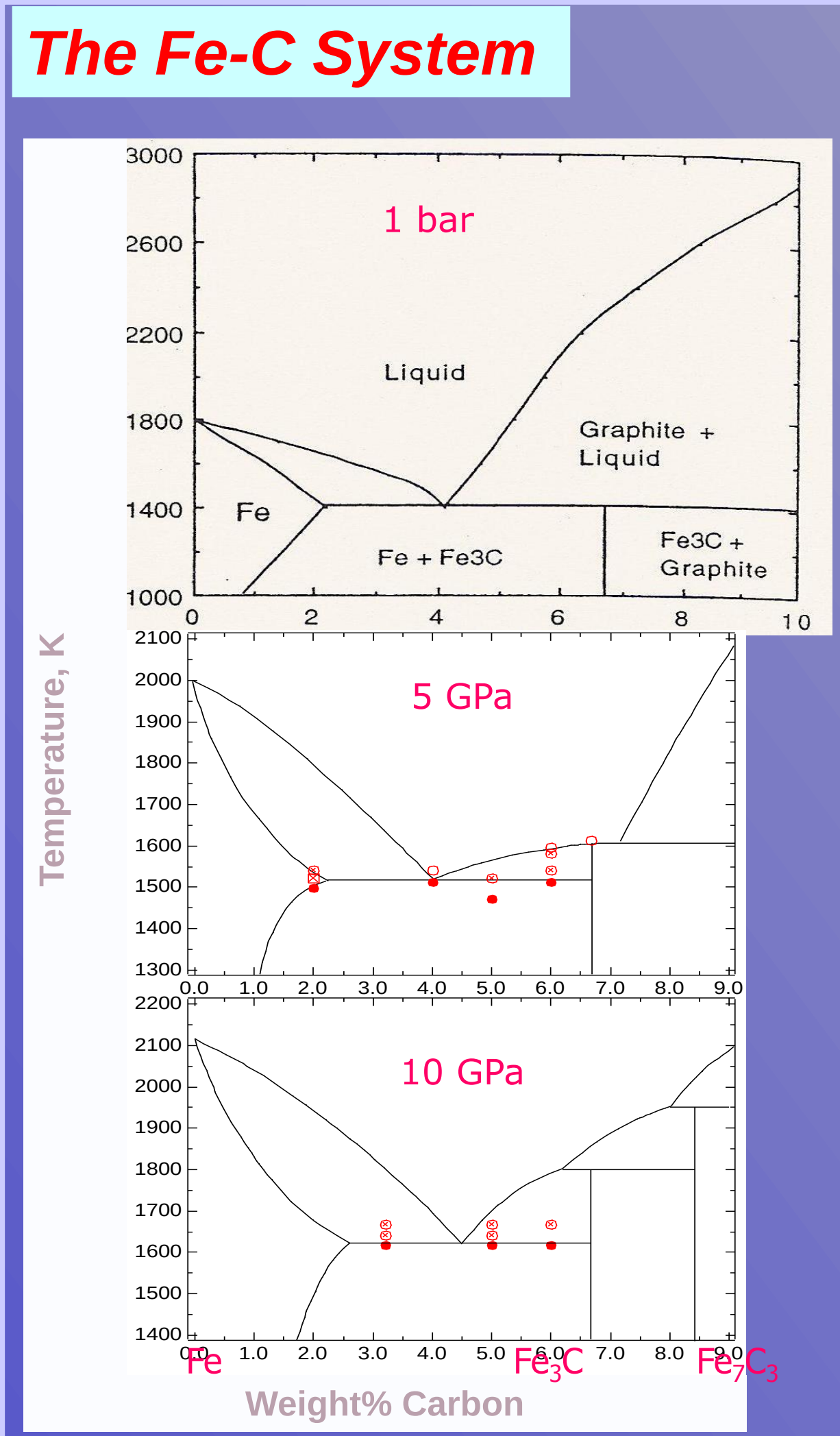


Fig. 6. Melting relations as a function of pressure in the Fe-C system.

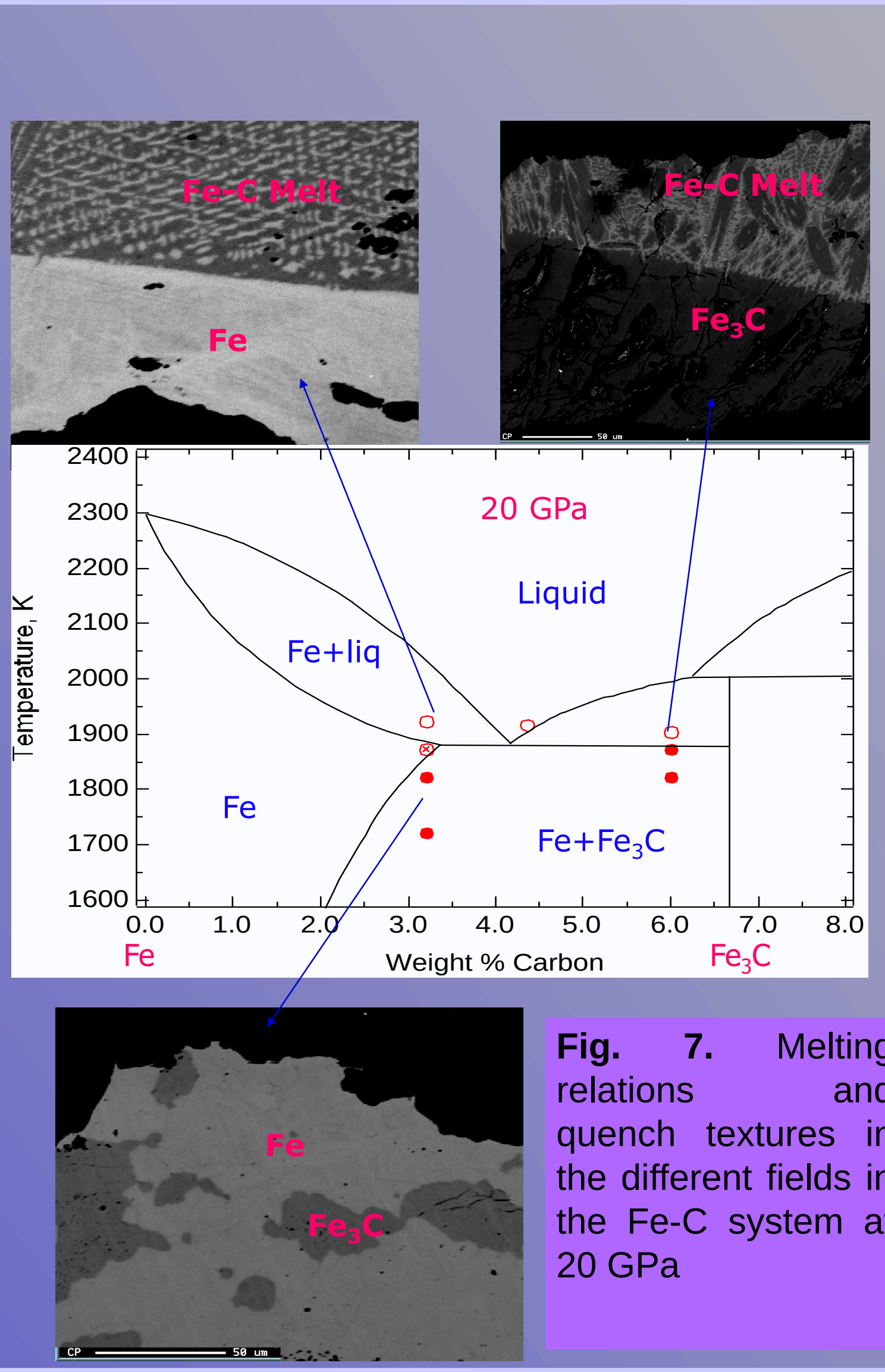


Fig. 7. Melting relations and quench textures in the different fields in the Fe-C system at 20 GPa

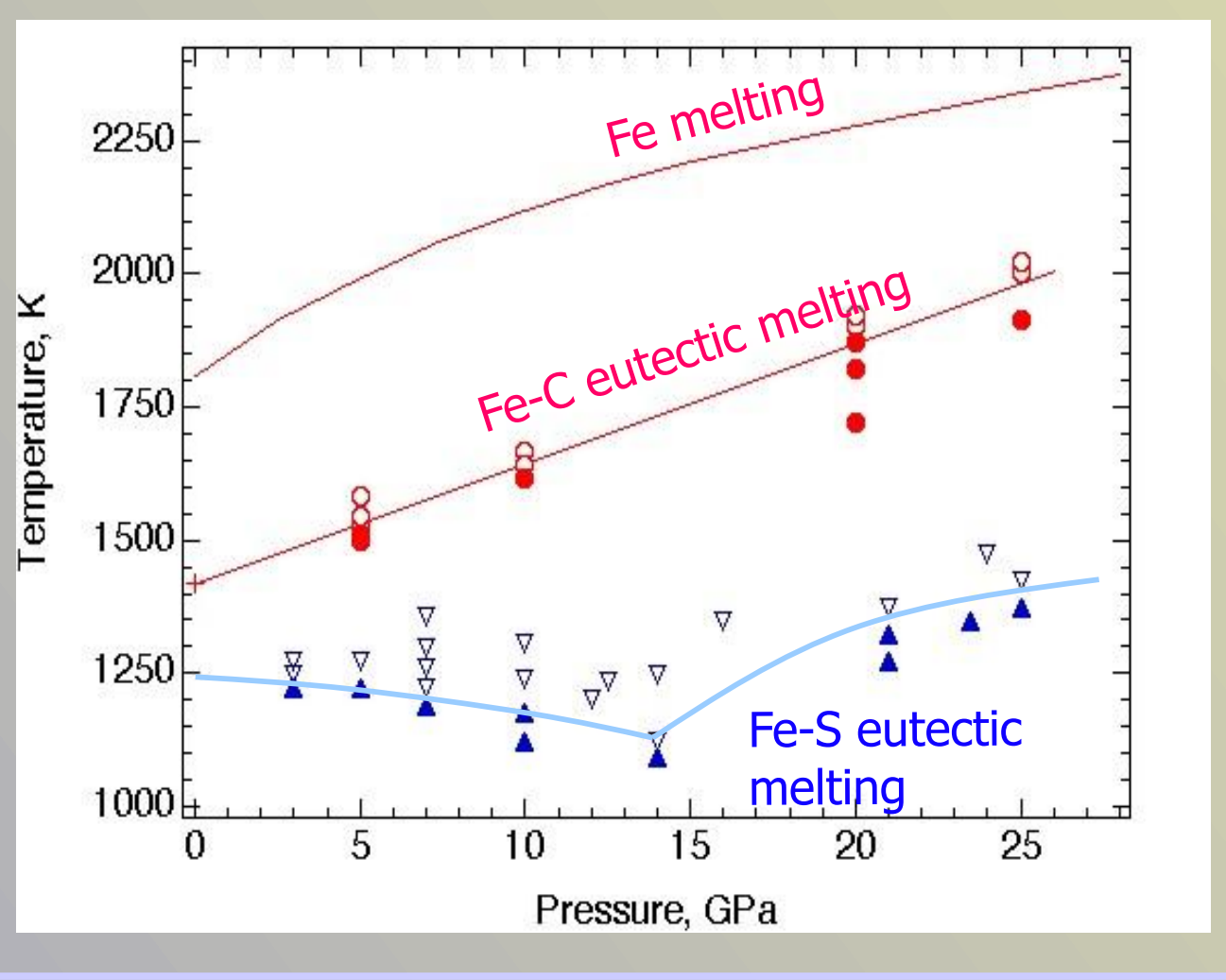


Fig. 8. Eutectic temperature as a function of pressure in the Fe-C system. The eutectic melting in the Fe-FeS system and Fe melting curve are also plotted for comparison. The Fe-S eutectic melting is significantly lower than that of the Fe-C eutectic melting. Both systems substantially low the melting temperature of pure iron, which will affect the temperature estimate of the planetary cores, depending on the amount of light elements in the cores.

The Fe-C-S System

The problem of light elements in the cores has to be address in multi-element system as various light elements were incorporated into the core during the differentiation process. The relative amounts of different elements in the core are governed by element partitioning and melting relations in the multi-component system at high pressure and temperature under different oxygen fugacity. Adding a small amount of carbon into Fe-S will cause a vast liquid immiscibility gap, which may have great effect on the melting relationship of the Fe-C-S ternary system. We have begun an experimental study in the Fe-C-S system at high pressure and temperature, with implication for evolution of the planetary core.

At low pressure (P < 5 GPa), we observed two immiscible C-rich and S-rich Fe-C-S liquids at 1873 K (Fig. 9). As temperature decreases, Fe_3C crystallizes, coexisting with a Fe-C-S melt. At P > 5 GPa, we observed only one Fe-C-S liquid, indicating miscibility gap closure at about 5 GPa (Fig. 9).

Our experimental results in the Fe-C-S system should provide necessary information for understanding core evolution in differentiated planetary bodies with the cores containing both S and C. The observed S-rich and C-rich immiscible liquids at low pressures (< 5 GPa) would lead to a stratified core for a small planetary body, with denser C-rich liquid inner core and S-rich liquid our core. As the core cools down, the C-rich liquid would crystallize Fe_3C first and then coexisting Fe_3C and metallic Fe. Significantly lower temperature is required to solidify the S-rich melt. For planetary core that is sufficiently large so that the core pressures are greater than 5 GPa, no composition stratification in the core is expected. Based on crystallization sequence, iron carbide or metallic iron would crystallize depending on the initial Fe/(C+S) ratio. With 90%Fe in the starting materials, iron carbide is the liquidus phase. In order to crystallize metallic iron with dissolved carbon, it is necessary to increase the initial Fe/(C+S) ratio. If the Earth's core contains both carbon and sulfur, the solid inner core is nearly S-free, but it could contain significant amount of carbon (Fig 10). On the other hand, the liquid outer core would be S-rich and C-poor.

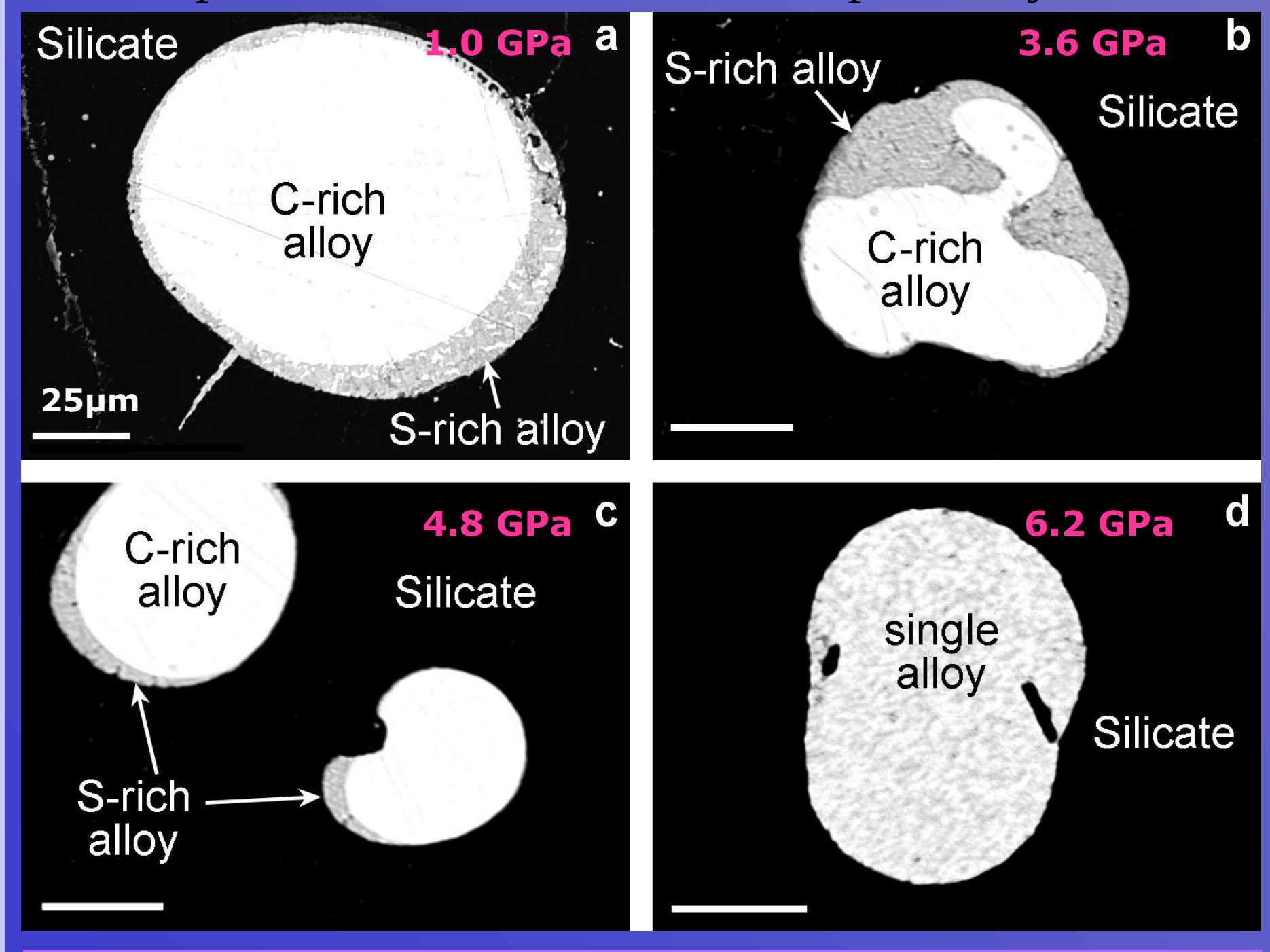


Fig. 9. Back-scattered electron images summarizing typical phase textures. (a) 1.0 GPa – 1700 ºC; (b) 3.6 GPa – 2000 ºC; (c) 4.8 GPa – 2000 ºC; (d) 6.2 GPa – 2000 ºC. At pressures below 5 GPa, molten silicate coexists with S-rich and C-rich molten alloys. At pressures above 5 GPa, there is complete miscibility and one single alloy is present.

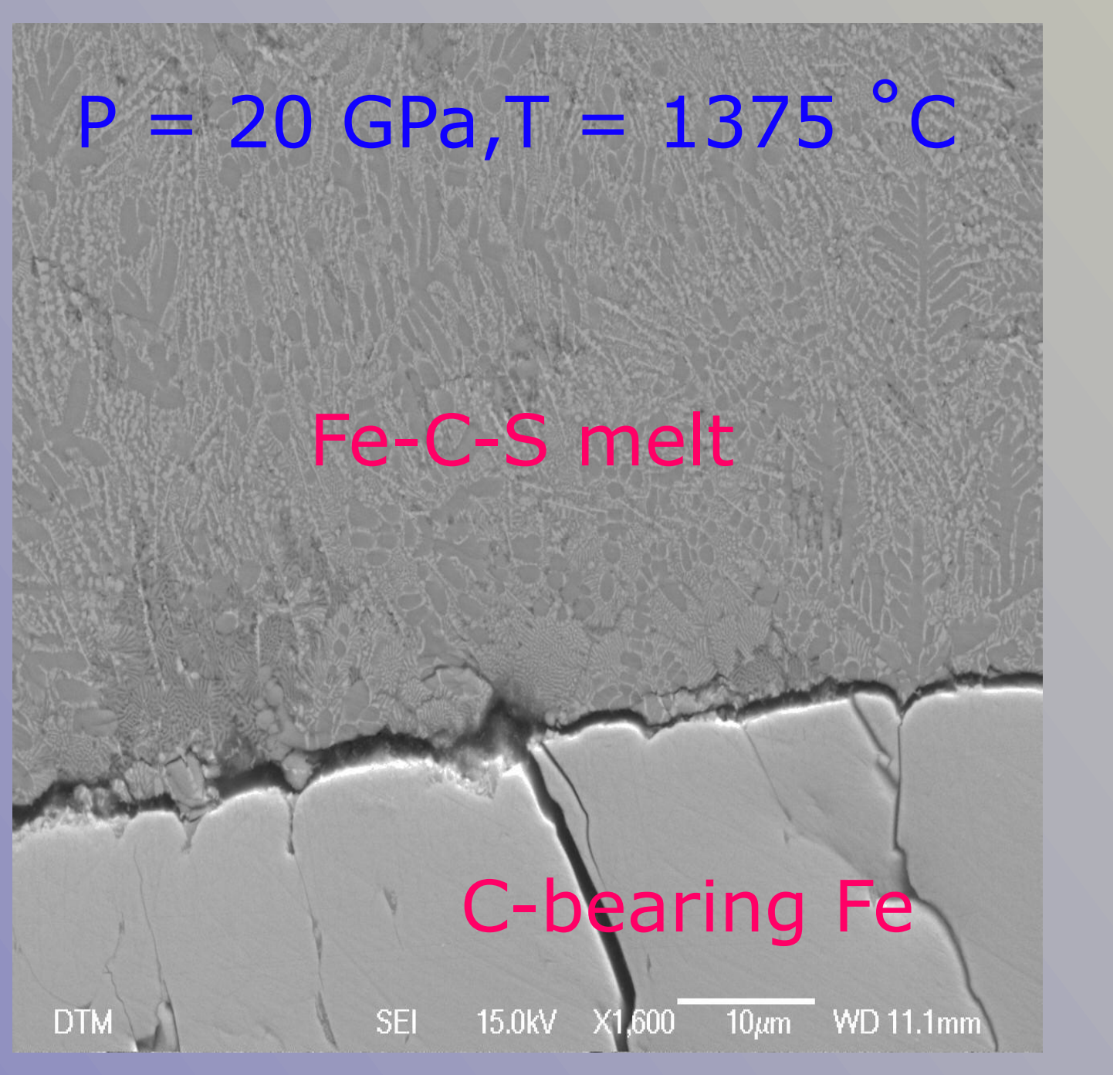


Fig. 10. Melting in the Fe-C-S system at 20 GPa. The solid contains C, but nearly S-free whereas the liquid is S-rich and C-poor.

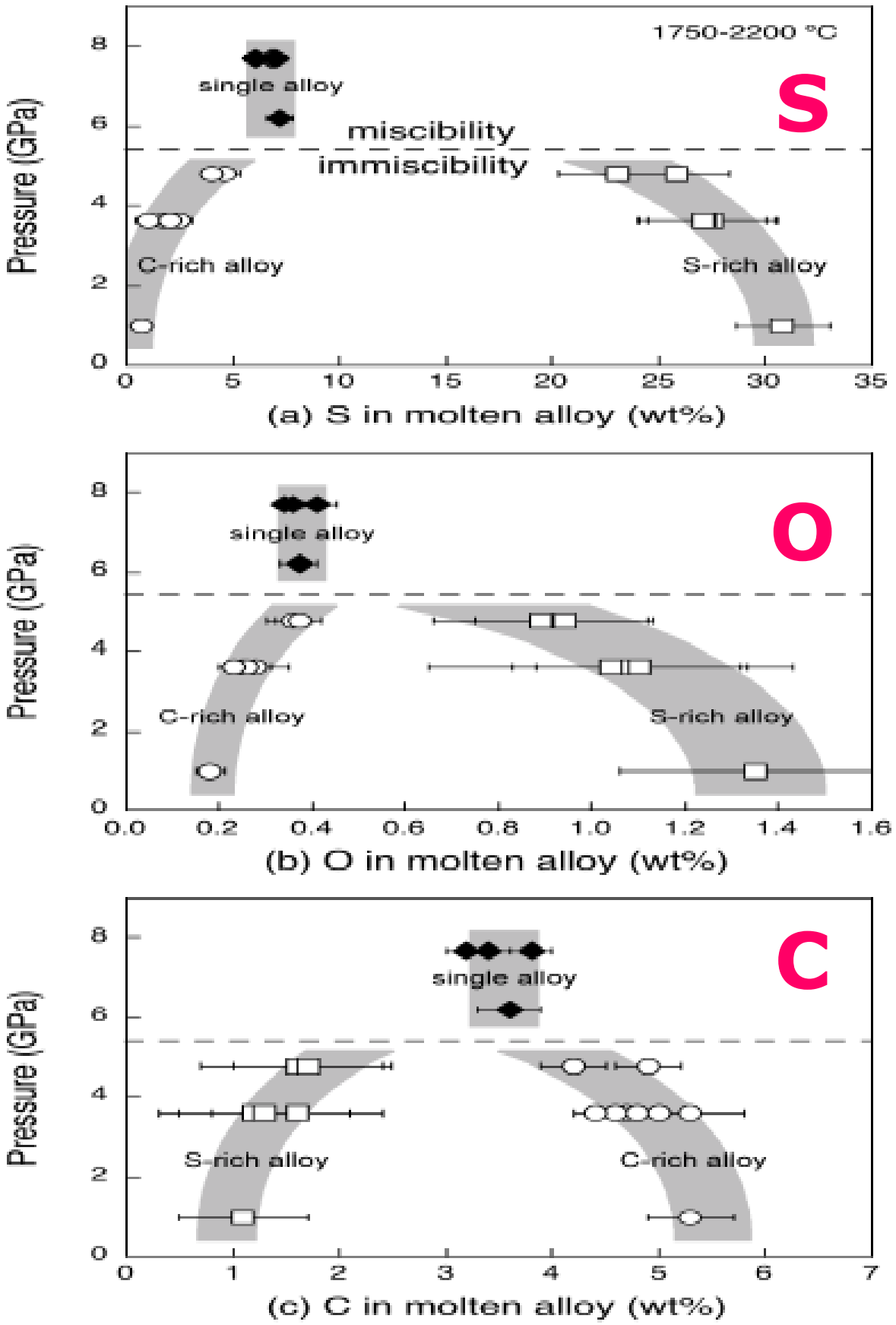


Fig. 11. Variation of the S, O and C contents of molten alloys with pressure.