Reports

Retrograde Melting in the System Mg-Fe-Si-O

Abstract. *Under certain limits of oxygen fugacity and temperature in the system Mg-Fe-Si-O the crystalline assemblage of olivine, tridymite, and metallic iron will produce liquid with cooling. Changes in composition, accompanying changes in temperature, of the olivine phase cause exothermic oxidation of the metallic iron, providing enough heat to produce liquid.*

Cooling the crystalline assemblage olivine, silica, and metallic iron under increasing, constant, or slightly decreasing oxygen fugacity leads to the formation of liquid at temperatures and oxygen fugacities (fO_2) between 1305°C, $10^{-11.3}$ atm and 1180°C, $10^{-12.7}$ atm at 1 atm of total pressure. The phenomenon will persist between different limits of temperature and oxygen fugacity (T-fO_2) up to approximately 17.5 kbar of total pressure.

Figure 1 illustrates a portion of the T-fO_2 projection of the system Mg-Fe-Si-O at 1 atm of total pressure (*1*). The lines 1, 2, 3, and 4 illustrate respectively, cooling under conditions of increasing, constant, slightly decreasing, and sharply decreasing oxygen fugacity. Cooling the assemblage in the area olivine + silica + iron along lines 1, 2, or 3 results in movement to the line representing conditions for the assemblage olivine + silica + iron + liquid. The mechanism leading to retrograde melting is simple and possibly far-reaching in its implications. Effectively, it is controlled by addition of oxygen to the bulk composition of the condensed phases.

Figure 2 illustrates the composition of the olivine in mole percent of fayalite in portions of the T-fO_2 projection for the various assemblages in Fig. 1 (*1, 2*). The minimum amount of fayalite present in olivine in the assemblage olivine + silica + iron is Fa_{68}, present at Q. Olivine in this assemblage becomes more iron-rich with cooling under all conditions of changing oxygen fugacity except with sharply decreasing fO_2, for example, line 4 in Fig. 1 (*3*). The process consists of addition of oxygen by oxidation of the metallic iron, combination of the resulting Fe^{++} with SiO_2 to form fayalite, and mixing of the fayalite with the olivine. The reactions along lines 1, 2, and 3 of Fig. 1 stop with a change of assemblage: either silica or iron disappears or the T-fO_2 path reaches one of the isobaric univariant boundaries where another phase appears, either the liquid or pyroxene phase. Theoretically, the T-fO_2 path for cooling the assemblage olivine + silica + iron can never reach the ternary boundary curve for fayalite + silica + iron, which extends to lower temperatures than q, because Mg^{++} is present and the reaction will stop with the disappearance of silica or iron before reaching it. Olivine, the only phase containing Mg^{++}, must remain.

The heat of reaction for the assemblage along the curve Q-q (Fig. 1) expressed as

$$(Mg,Fe)_2SiO_4 + SiO_2 + Fe^\circ + mO_2 = \text{liquid} + nO_2$$

is a combination of heat of fusion and heat of oxidation, where the difference, m-n, is 1 gram-atom of oxygen. The slope of the curve indicates a value for the combined reaction of approximately 114 kcal. The heat released by

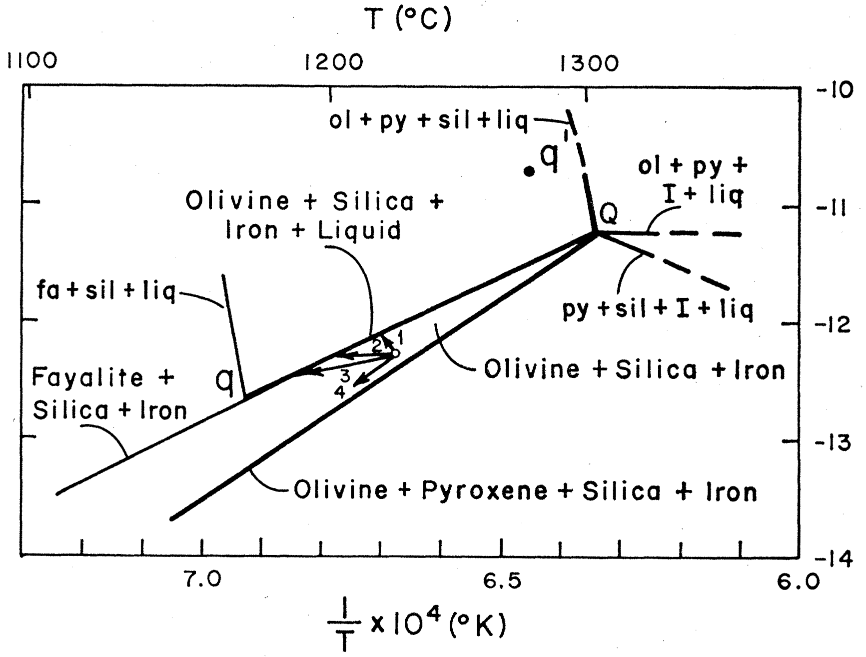

Fig. 1. A portion of the T-fO_2 projection of the system Mg-Fe-Si-O at 1 atm total pressure, illustrating the stabiliy field for the assemblage olivine + silica + iron (*1*). Heavy lines indicate isobaric univariant conditions for various assemblages. The phases present are spelled out for assemblages of immediate interest, abbreviated for others. The isobaric invariant point Q represents conditions for the assemblage olivine + pyroxene + silica + iron + liquid. Light lines indicate isobaric univariant conditions for assemblages in the limiting ternary, Fe-Si-O (*6*). The ternary isobaric invariant point q represents conditions for the assemblage fayalite + silica + iron + liquid (*7*). For comparison, point q' represents invariant conditions for the assemblage ferrosilite + fayalite + silica + iron + liquid with a total pressure of 17.5 kbar (*1, 5*). Cooling curves at increasing, constant, slightly decreasing, and sharply decreasing fO_2 are labeled 1, 2, 3, and 4, respectively. Cooling curve 4 also corresponds to cooling at constant bulk composition. Abbreviations: *ol*, olivine, *py*, pyroxene; *sil*, silica; *liq*, liquid; *I*, metallic iron; *fa*, fayalite.

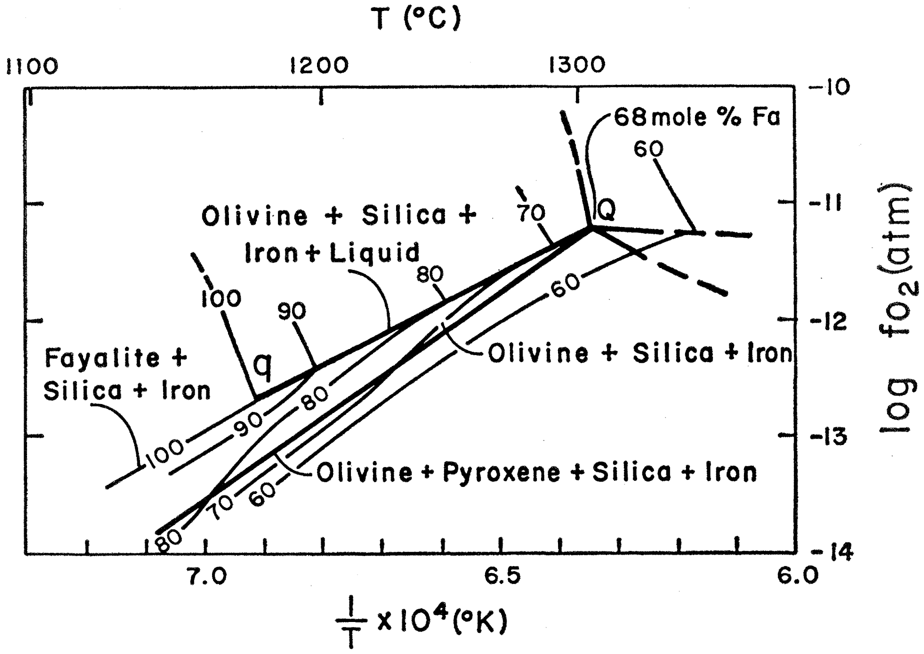

Fig. 2. Composition of olivine (mole percent of fayalite) in portions of the T-fO_2 projection for the various assemblages in Fig. 1. Unlabeled boundary curves and other information are defined in Fig. 1.

the oxidation of metallic iron to Fe^{++} per gram-atom of oxygen is 63 kcal (*4*). Thus, the addition of less than 2 gram-atoms of oxygen, changing the bulk composition, provides enough heat of oxidation to exceed the heat of fusion for the new bulk composition.

This phenomenon will exist up to the pressure for the stability of ferrosilite in the assemblage fayalite + silica + iron + liquid, determined to be at 17.5 kbar total pressure (*5*) and represented for comparison with the relations at 1 atm total pressure by the point q' in Fig. 1. The points Q and q move towards q', which is an invariant point in the limiting ternary Fe-Si-O, with increasing pressure as the amount of Fe^{++} in the pyroxene phase increases to $FeSiO_3$. The spatial relations of the assemblage olivine + silica + iron + pyroxene to olivine + silica + iron + liquid are expected to remain similar, that is, a portion of the stability field olivine + silica + iron remains on the high-temperature side of the curve Q-q. The stability field of olivine + silica + iron disappears under pressures greater than 17.5 kbar.

The phenomenon described could be expected to be present in a two-metal–oxide–silicate system, where the oxidation of the metal is exothermic, if at least one of the metals present has a variable oxidation state and the composition of the silicate phase becomes enriched in that metal with cooling. Metals such as Ni, Co, and Mn could be expected to show similar behavior. This type of process and the energies involved should be considered in any discussion of reactions where metallic iron or possible Fe-Ni-Co-Mn alloys coexist with ferromagnesium silicates. An immediate suggestion is that the apparent localized melting in meteorites with little or no obvious sources of radioactive heat might possibly be caused by this process.

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References and Notes

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3. Along line 4, Fig. 1, olivine is constant in composition, the bulk composition of the condensed phases is constant, and the mechanism does not apply. Cooling the assemblage under constant composition conditions with olivine containing between Fa_{68} and Fa_{80} will lead to the formation of pyroxene and with further cooling will lead either to the assemblage olivine + pyroxene + iron or pyroxene + silica + iron, depending on the ratios of Mg: Fe: Si of the bulk composition.
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8. We thank Professors A. Muan and E. F. Osborn for review of the manuscript. Supported by NSF and AEC.

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High-Purity Calcium Carbonate in Freshwater Clam Shell

Abstract. *The calcium carbonate in freshwater clam shells is similar in purity to that designated reagent grade. A simple reprecipitation of the shell extract results in a product having less Sr and Mg than reagent grade $CaCO_3$. Clams are harvested commercially, and discarded shells are a high-quality raw material for the production of $CaCO_3$.*

Biogeochemical prospecting is a generally accepted technique based on an anomalous distribution in the environment of chemical elements created by organisms. Most investigations have been concerned with abnormal chemical concentrations in plants or plant parts (*1*). Utilization of knowledge of biogeochemical relationships among plants and their environment has obvious economic implications in locating subsurface ore deposits. Another facet of biogeochemistry that may be of economic importance is the metabolic discrimination against trace elements in biogenic calcareous materials. The biogenic materials, such as clam shell, are a renewable natural resource rather than an exhaustible one, such as ore bodies. The purpose of this paper is to compare trace element concentrations in commercially available reagent grade $CaCO_3$ with those deposited in freshwater clam shell and to suggest clam shell as a possible commercial source of $CaCO_3$.

The distribution of stable Sr in clam shells was studied in connection with the behavior of ^{90}Sr in the Clinch and Tennessee rivers (*2*). Because of the low Sr concentration in freshwater clam shell, a new analytical technique was developed to measure accurately Sr concentrations in calcareous material (*3*). When Sr concentrations in unpurified clam shell and reagent grade $CaCO_3$ were compared, it was apparent that $CaCO_3$ from clam shell was of equal or better purity.

The clam shells were ashed in a muffle furnace at 800°C for 2 hours. A portion (1 to 5 g) of the ash was transferred to a 250-ml beaker and dissolved in 2*M* HCl. The solution was transferred to a 100-ml volumetric flask and diluted with water to calibrated volume. Portions were taken from this solution and element concentrations were determined by flame emission spectrophotometry (Table 1). All data were confirmed by an emission spectrographic method (*4*).