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ON THE ELECTROCHEMICAL ORIGIN OF NATURAL GRAPHITE

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Abstract

The hypothesis is advanced that pyrrhotite, an accessory mineral, could electrochemically control the deposition of natural graphite from an aqueous solution of carbon dioxide. It could do this as a simple short-circuited voltaic cell under moderate solution temperatures and pressures.

Discussion

The origin of natural graphite is a geochemical problem of some importance. In many occurrences, isotopic evidence (Craig, 1953) suggests an inorganic source of the carbon, namely carbon dioxide or carbonates. Because of the exceptional temperature stability of carbon dioxide, a reducing agent seems needed for the conversion to graphite.

It may be more than coincidence that one of the most electronegative and electroconductive minerals, pyrrhotite, is so frequently mentioned as an accessory mineral in graphite deposits. Rankama (1948) even has stated that in Finland "pyrite and pyrrhotite occur in carbon-bearing schists almost invariably, irrespective of their degree of metamorphism". As a simple short-circuited voltaic cell, the possibility exists for pyrrhotite to control the electrodeposition of graphite from an aqueous solution of carbon dioxide. Voltaic cells are not uncommon in nature. They account for the self-potential anomalies associated with sulfide ore bodies (Sato and Mooney, 1960).

The reduction of carbon dioxide to carbon monoxide, the first step in a reduction process, is thermodynamically less favored than the reduction of water to hydrogen. It is difficult, therefore, to electrochemically reduce carbon dioxide in an aqueous solution. High hydrogen-overvoltage electrodes are necessary for the direct reduction and at potentials exceeding the electrode potential of pyrrhotite or any other mineral system. However, water can be electrochemically reduced to chemisorbed hydrogen at cathode potentials up to 300 mV more positive than the hydrogen gas evolution potential at 25°C (Giner, 1963; Breiter, 1967). This labile intermediate species is then able to react with carbon dioxide reducing it to chemisorbed carbon monoxide.

The continued reduction of chemisorbed carbon monoxide on the platinum electrodes used by Giner and Breiter was not observed by them. Bianchi, *et al.*, (1958), however, have postulated the two step reduction of CO_2 to C on a graphite electrode in an aqueous solution at 25°C based on the cathodic polarization curves they obtained. Their work remains to be verified.

Understandably, the reduction of CO to graphite would involve a large activation energy although thermodynamically it is more favored than either the reduction of water or carbon dioxide. Moderate solution temperatures, above 70°C, would enhance the reduction as Giner found in his studies. These hydrothermal conditions are common and could have prevailed during the formation of graphite.

Electrode potential measurements by Sato (1960) indicate some difference between the oxidation potentials of natural and synthetic pyrrhotite. Taking an average value of the experimental potentials, $Eh = -0.1$ V at pH 7 and 25°C, pyrrhotite could electrochemically reduce water. There is still much uncertainty as to the specific half-cell reaction responsible for the oxidation potential of pyrrhotite at 25°C. In addition, there is no data on the electrode potential at elevated temperatures.

Once a monolayer or nucleus of graphite is deposited on a cathodic region of the pyrrhotite, subsequent reduction of the carbon dioxide could be catalyzed by the graphite. Not only is direct chemical reduction of carbon dioxide to adsorbed carbon monoxide a possibility at moderate solution temperatures (Tee and Tonge, 1963), graphite provides the ideal substrate geometry to effect the CO to C reduction.

The electrocrystallization of graphite could explain many features of natural graphite, particularly vein graphite where "mineralization is confined to late fractures and shears devoid of associated gangue or introduced minerals" (Ford, 1954). Voltaic action would permit control of graphite crystallization from small pockets of pyrrhotite at some distance from the growing crystal-solution interface. This would explain the low concentration of gangue minerals and a graphite mineralization typical of open vein fillings from solution (Bastin, 1912). An electrolytic mechanism also could explain the large crystal dimensions and the many variations from a regular crystal structure that are observed. The electrodeposition would be diffusion-controlled, favoring large crystals. Concentrations, current density, and temperature could vary considerably during the long period of deposit formation. Crystal structure variations could reflect this as they do in the electrodeposition of metals.

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SUBSOLIDUS PHASE RELATIONS IN THE SYSTEM CALCIUM CARBONATE–CADMIUM CARBONATE

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ABSTRACT

In the temperature range 400°–750°C, a miscibility gap of aragonite- and calcite-type phases forms in the Ca rich portion at 15 kbar. It diminishes in range with decreasing pressure, and at 10 kbar a complete series of solid solutions of the calcite-type structure was found.

Variation of lattice parameters of the solid solution series was calculated as a function of binary composition, and *c* shows a positive deviation from the Vegard's law.

Subsolidus phase relations among calcite-type carbonates have been studied extensively in recent years, but for the system $CaCO_3$–$CdCO_3$, equilibrium relationship has not been satisfactorily established. Because the two divalent cations involved in the system are of almost identical ionic size and distinct electronic structure, this system is of interest especially in three aspects; the effect of cadmium on the calcite-aragonite