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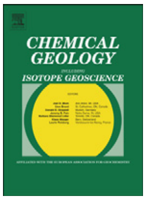

Melting of siderite to 20 GPa and thermodynamic properties of $FeCO_3$-melt

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ABSTRACT

The siderite ($FeCO_3$) melting curve is determined through multi-anvil experiments at 6–20 GPa, and 1300–1870 °C. The experiments define a melting curve with a Clapeyron slope steepening from 45 to 18 °C/GPa but without backbend at upper mantle conditions, i.e., siderite is denser than $FeCO_3$-melt ($FeCO_3L$). The melting curve fits $T_m = 1037(44) + 70.0(88) * P - 1.43(37) * P^2$ (valid from 5 to 20 GPa) where pressure is in GPa and temperature in °C. Siderite melting is not stoichiometric, minor quench magnetite was always observed and is interpreted as the result of partial redox dissociation of $FeCO_3L$ leading to dissolved Fe^{3+} and CO_2 in the carbonate melt. At pressures below ~6.8 GPa, siderite does not melt but decomposes through an auto redox dissociation reaction to magnetite, a carbon polymorph and CO_2. From the experimental determination of the pure siderite melting curve, we calculate thermodynamic properties of the $FeCO_3L$ end-member, which reproduce the siderite melting curve in P–T space better than 10 °C. The metastable 1 atm melting temperature is calculated to 1012 °C. Siderite has the lowest melting temperature of the Ca–Mg–Fe carbonates, its melting curve may cross the mantle geotherm at transition zone pressures. The stability of siderite is not only dependent on pressure and temperature but also strongly on oxygen fugacity (fO_2). Model calculations in P-T-fO_2 space in a Fe–C–O_2 system show that the siderite or $FeCO_3$-melt maximum stability is always reached at conditions of the CCO buffer. Our experimental and thermodynamic data constitute a cornerstone to model carbonate melting in the deep Earth, necessary to understanding the deep carbon cycle.

1. Introduction

Carbon is a major and vital component in the geological rock record. It occurs in oxidized form as CO_2 and carbonate, as elemental carbon (graphite or diamond) and metallic phases (e.g., Fe_3C), or in its reduced state, mostly as organic material but also as CH_4 or hydrocarbon species in reduced fluids. The majority of the Earth's surface carbon is sequestered in carbonates contained either in sedimentary rocks or in the altered oceanic crust. Ocean floor metamorphism enriches the oceanic crust with CO_2 through precipitation of carbonates (Staudigel, 2003). The transport and storage of carbon within the mantle influence the global carbon budget via volcanic CO_2 release to the atmosphere and subsequent cycling back into the mantle by subduction of oceanic sediments and carbonated peridotitic and mafic rocks (Sleep and Zahnle, 2001). In general, most of the subducted carbonate is believed to descend beyond subarc depth, this in contrast to hydrous phases, whose larger part decomposes and generates H_2O-rich fluids at subarc conditions (Connolly, 2005; Poli et al., 2009). As a result, carbon-bearing minerals are transferred to deeper mantle regions. These are documented as carbonate inclusions in natural diamonds (e.g. magnesite) and carbonate minerals in mantle xenoliths (Pal'yanov et al., 1999).

The modern C-cycle is characteristic for an Earth with an oxygen-rich atmosphere. Before the first rise of oxygen ~2.3 Ga ago, lithologies such as banded iron formations (BIFs) and anoxic shales were much more abundant and constituted common deep sea and platform sediments of anoxic oceans (Klemm, 2000). BIFs, mostly composed of quartz + hematite + magnetite are frequently also rich in organic carbon (Beukes and Gutzmer, 2008). The latter reacts with the iron oxides upon low grade metamorphism to siderite ($FeCO_3$) or ankerite ($CaFe(CO_3)_2$). Most of these ancient sediments, especially deep sea BIFs, were subducted in the Archean (Kusky et al., 2001; Polat et al., 2002). To understand this process, the high-pressure behavior of siderite needs to be characterized. The “pure”, simple BIF system SiO_2–FeO–Fe_2O_3 is refractory and melts only at 1455 °C at 1 atm (Phillips and Muan, 1959). The addition of carbon and hence of siderite or ankerite is expected to strongly reduce such melting temperatures.

Understanding carbonate stability at mantle conditions is also crucial under other aspects: First, for the carbon cycle itself, secondly, because at high pressures carbonate-bearing silicate rocks have lower melting temperatures than those with only silicates, and third, because

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carbonatitic magmas are highly mobile and enriched in trace elements, their transfer modifying the geochemistry of deep mantle domains. In this context, the $CaCO_3$–$MgCO_3$–$FeCO_3$ ternary constitutes the most basic system for carbonates and carbonate melts and is a key to predict melting relations even in any more complex system, since natural carbonatites are dominated by (Ca, Mg, Fe^{2+})-components.

The first experimental study in the Ca–Mg–Fe-carbonate ternary described subsolidus phase relations at 600–800 °C, 1.5 GPa (Goldsmith et al., 1962). Below 700 °C, Goldsmith et al. (1962) determined a 3-phase field consisting of coexistent Fe–dolomite, Fe–calcite and Mg–siderite. Furthermore, Rosenberg (1967) investigated this ternary at temperatures between 350 and 550 °C at 0.2–0.3 GPa and confirmed the presence of the above 3-phase field. Finally a complete ternary solid solution model for carbonates to 1100 °C, 3.5 GPa was formulated by Franzolin et al. (2011) on the basis of additional experiments.

Regarding end-members of the $CaCO_3$–$MgCO_3$–$FeCO_3$ system, Irving and Wyllie (1975) experimentally constrained the melting reaction of pure calcite at 1, 2 and 3 GPa to ~1430, 1550 and 1610 °C. Suito et al. (2001) determined $CaCO_3$ melting temperatures of ~1730 °C at 4–6 GPa and ~2000 °C at 8 GPa and proposed a melting curve for disordered calcite. Congruent melting of pure magnesite is observed at 1585 to 1620 °C at 3 to 3.6 GPa (Irving and Wyllie, 1975) and at 8 to 15 GPa at ~1950 and ~2050 °C, respectively (Katsura and Ito, 1990). Note that these data suggest that the calcite and magnesite melting curves cross at ~5 GPa.

Experimental data on the phase relationships of siderite at high pressure are limited and thermodynamic data of melt of siderite composition ($FeCO_3L$) are completely lacking. The system Fe–C–O_2 has been studied experimentally to 1.5 GPa and 700 °C (French, 1971; Weidner, 1972; Koziol, 2004). More recently, Tao et al. (2013) investigated the siderite stability field to 10 GPa by multi-anvil experiments. For comparison, calcite melt becomes stable at pressures greater than a few hundred bar, magnesite melt only stabilizes at ≥ 2.7 GPa (Irving and Wyllie, 1975), while siderite melt requires between 7 and 8 GPa (Tao et al., 2013).

The present study provides experimental data for the siderite system from 6 to 20 GPa in the temperature range of 1300–1870 °C. The purpose is to understand the stability of siderite as a function of oxygen fugacity and to constrain the thermodynamics of $FeCO_3L$. The $FeCO_3L$ data can be applied e.g. to predict the melting behavior of carbonated banded iron formations, an alkali-free, chemically relative simple system, which once was that of a common sediment.

2. Previous experimental phase relations of Fe-rich carbonates and siderite

Phase equilibria in the Fe–C–O_2 system (Fig. 1) have been investigated by few experimental studies aiming at the origin of Fe-rich carbonatites and at BIFs and their metamorphosed equivalents. Siderite is a common constituent of low-grade sedimentary iron formations and hydrothermal veins. Most natural siderites contain significant amounts of Mg^{2+} and Mn^{2+} and are commonly associated with iron-rich dolomite or ankerite. Upon thermal dissociation of carbonates such as calcite, magnesite and smithsonite ($ZnCO_3$), their cations do not oxidize (Harker and Tuttle, 1955). However, several investigations show that siderite is not stable under atmospheric conditions (Smythe and Dunham, 1947; Holland, 1965; Seguin, 1966; French, 1970). Natural siderite converts to iron oxides or hydroxides upon exposure to the atmosphere or to near-surface ground waters (Silliman, 1820; Burchard, 1924). In the Fe–C–O system siderite may either decompose through a simple decarbonation reaction:

$$1\ \text{siderite} = 1\ \text{wüstite} + 1\ CO_2 \tag{1}$$

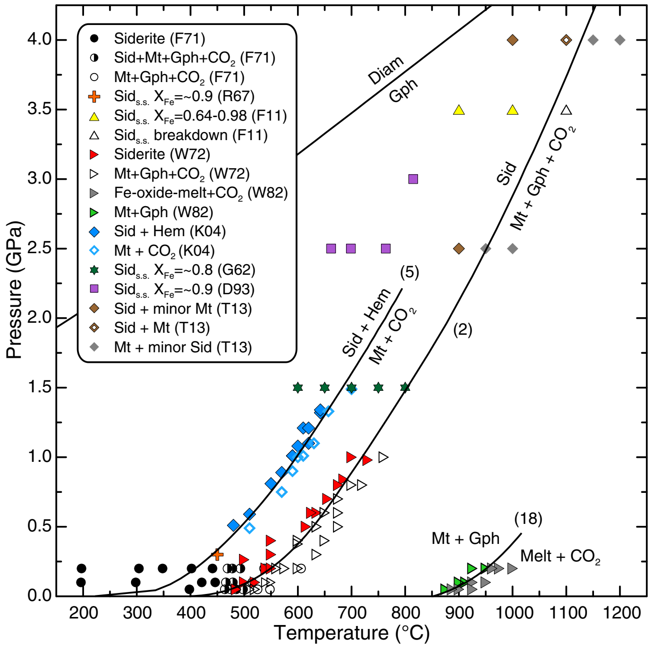

Fig. 1. *P*–*T* diagram compiling subsolidus experiments on siderite, also including the few experiments on Ca–Mg–Fe carbonates and calcite–siderite solid solutions with $X_{Fe} = 0.64$–0.98. The terminal stability of siderite is defined by redox dissociation to magnetite + graphite + CO_2 (reaction 2, the curve is a visual fit to the data). Reaction 5 is calculated with our siderite data. Weidner (1982) determined the low pressure minimum melting reaction (18) in Fe–C–O at low pressures. F71: French, 1971, R67: Rosenberg, 1967, F11: Franzolin et al., 2011, W72: Weidner, 1972, W82: Weidner, 1982, K04: Koziol, 2004, G62: Goldsmith 1962, D93: Davidson et al., 1993, T13: Tao et al., 2013. Hem = hematite; Sid = siderite; $Sid_{s.s.}$ = siderite solid solution; Mt = magnetite; Gph = graphite; Diam = diamond; C = carbon; $FeCO_3L$ = melt of almost $FeCO_3$ composition; Lc = carbonate quench; AuPd = gold-palladium capsule alloy; Wu = wustite; IronL = iron melt; HM = hematite–magnetite buffer; CCO = graphite-CO_2 buffer; MW = magnetite–wustite buffer; WI = wustite–iron buffer. (Color online.)

or through a redox-dissociation reaction:

$$6\text{siderite} = 2\ \text{magnetite} + 1\ \text{graphite} + 5\ CO_2 \tag{2}$$

(Fig. 1), this latter univariant reaction delimits siderite stability at low pressures. Reaction 2 was studied by French (1971) in the system Fe–C–O_2 between 50 and 200 MPa in a CO_2 + CO atmosphere as a function of T, $P_F(=P_{CO2} + P_{CO})$. Further high pressure cold-seal experiments on this reaction were conducted by Weidner (1972) from 0.05 to 1 GPa and 450 to 760 °C, employing pure siderite as a starting material. The equilibrium curve (reaction 2) is characterized by a slight change in slope at ~0.45 GPa and 600 °C, which was interpreted as a non-quenchable polymorphic transformation in siderite (Weidner, 1972). Most recently, reaction 2 was determined at 2.5–6 GPa where it has a Clapeyron slope of about 0.0082 GPa/K (Tao et al., 2013). This latter study found siderite + magnetite to melt at 1500 °C, 8 GPa and 1550 °C, 10 GPa.

Equilibrium reaction 2 constrains oxygen fugacity to the CCO buffer, which implies that CO may occur as a species, either via the equilibrium

$$2\ CO = 1\text{graphite} + 1CO_2 \tag{3}$$

or directly through decomposition of siderite

$$3\ \text{siderite} = 1\text{magnetite} + 2\ CO_2 + 1CO \tag{4}$$

(French and Rosenberg, 1965). Nevertheless, the molar fraction of CO at high-pressure conditions is vanishingly small and calculated to be 0.29 10^{-3} at 10 GPa, 1500 °C, such that CO will no longer be discussed here.