



Solids and liquids in the (Fe, Mg, Ca)S-system: experimentally determined and thermodynamically modelled phase relations

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Abstract

Thermodynamic descriptions and experimentally verified phase relations in the FeS-MgS-CaS system are important both for steelmaking and for natural reduced systems. Experimental and thermodynamic data for such oxygen-poor systems are sparse due to the difficulty of conducting experiments under conditions at which these sulfides are stable. In this study, phase relationships were determined for FeS-MgS at 1170–1550 °C, for FeS-CaS at 1025–1600 °C, for MgS-CaS at 900–1500 °C and for FeS-MgS-CaS at 1050 and 1360 °C. Experiments were performed in evacuated silica glass tubes with excess Fe⁰ to favour troilite (FeS) rather than pyrrhotite (Fe_{1-x}S) for the FeS-rich phase. Textural interpretations and measured compositions indicate that the FeS-CaS system melts eutectically at 1063 ± 3 °C at 7 ± 1 mol% CaS. The FeS-MgS system is also modelled to be eutectic (at 1180 and 2.5 mol% MgS), yet, experimentally, its eutectic or peritectic character could not be unequivocally determined. This system's liquidus has a higher dT/dX than previously reported. The MgS-CaS system was found to have a symmetric miscibility gap that closes at 1210 °C. Differences to the outcome of previous experimental studies can be explained by the presence of troilite rather than pyrrhotite in our experiments when Fe-rich solid solution coexists with liquid or solid solution. The experimental data are fit by a thermodynamic model that reproduces the experimentally determined phase relations, and is capable of predicting melting phase relations for the FeS-MgS-CaS ternary.

Keywords Niningerite · Troilite · Oldhamite · Sulfides · Phase equilibria · Mercury

Introduction

In terrestrial environments, sulfur most commonly forms sulfides with Fe, Ni, Zn or Cu (Sack and Ebel 2006) or sulfates, such as anhydrite (CaSO₄). Natural sulfur-bearing liquids tend to be near mono-sulfidic and FeS-rich with varying amounts of other chalcophile elements. The most abundant minerals are cubic pyrite (FeS₂) and monoclinic pyrrhotite, a solid solution of composition FeS to Fe_(1-x)S (x = 0 to 0.125) found in many magmatic rocks. Hexagonal troilite (FeS) is the major sulfur phase found in many meteorites such as chondrites (Lunning et al. 2020), iron meteorites (Oshtrakh et al. 2016) and achondrites (Rochette et al. 2001).

At quite reducing conditions, oxygen fugacity is sufficiently low as to result in the incorporation of nominally lithophile elements, such as Mn, Mg and Ca into sulfides (Kurat et al. 2004; Larimer 1968; Lodders 1996; Whitby et al. 2002). These phases, i.e. alabandite (MnS), niningerite (MgS) and oldhamite (CaS), crystallize in a NaCl cubic crystal structure (Skinner and Luce 1971), form solid solutions with each other (Dilner 2016; Dilner et al. 2016, 2015; Skinner and Luce 1971) and coexist with hexagonal or monoclinic FeS (Barraud et al. 2021; Nittler et al. 2011; Skinner and Luce 1971). The compositions of the liquid and cubic solid solutions of (Fe,Mg,Mn,Ca)S-phases (in the following ss_{cub}) are strongly temperature-dependent and may be used as thermometers for meteorites or planetary bodies (Skinner and Luce 1971).

The FeS-MgS-CaS system is of special importance to Mercury, where available data on surface composition by X-ray spectrometry (XRS) (Nittler et al. 2011; Weider et al. 2012), gamma-ray spectrometry (GRS) (Evans et al. 2012; Peplowski et al. 2012) and neutron spectrometry (NS) (Lawrence et al. 2013; Riner et al. 2011)) suggest exceptionally

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high sulfur contents of 1–6 wt% at low Fe-contents (Evans et al. 2012; Nittler et al. 2011; Starr et al. 2012; Weider et al. 2015; Weider et al. 2012). Sulfur contents have been found to correlate with Ca and to a lesser extent with Mg (Nittler et al. 2011; Weider et al. 2012), possibly indicating the stability of solid solution phases (Anzures et al. 2020).

Experimental work on the FeS-MgS-CaS system is scarce. In the following, we summarize the existing data.

FeS

Stoichiometric FeS is hexagonal troilite, but in nature and experiments monoclinic pyrrhotite $\text{Fe}_{(1-x)}\text{S}$ ($x = 0$ to 0.125) may form (see above). The melting temperature of the FeS endmember is hence somewhat uncertain and riddled by the problem of experimenting on stoichiometric troilite without metal saturation. A summary of earlier studies on FeS melting is given by Jensen (1942), 12 of 14 melting points are between 1163 and 1197 °C. Jensen (1942) found the maximum melting temperature of pyrrhotite to be 1190 °C at composition $\text{Fe}_{0.935}\text{S}_1$. A temperature of 1190 °C was also found by Zlomanov and Novoselova (1987), as cited by Andreev et al. (2006). On stoichiometric FeS, Jensen (1942) found melting to start at 1064 °C and end at 1171 °C, the solid evolving towards the above pyrrhotite composition with increasing temperature. This behaviour is consistent with the quite differing melting behaviour of FeS without and with Fe^0 saturation as e.g. reported by Mann and Van Vlack (1976) in the Mn-Fe-S ternary system where the metal-sulfide eutectic is found at 997 °C, the eutectic in pure Fe-FeS lying at 988 °C (Hansen et al. 1958). Later studies (D.T.A experiments in the Fe-S-Ag system) report higher melting temperatures for FeS (1192 ± 2 °C) (Taylor 1970), which was restated in large-grain troilite synthesis experiments (Moreau et al. 2022).

FeS-MgS binary

To our knowledge, the only study of melting in the FeS-MgS binary is by Andreev et al. (2006), who used visual polythermal analysis (VPTA) and differential thermal analysis (DTA), employing evacuated silica glass tubes and graphite crucibles. They report that the FeS-MgS binary system yields a peritectic reaction according to $\text{FeS ss} = \text{MgS ss}_{\text{cub}} + \text{liq}$, with a maximum solubility of 2 ± 0.5 mol% MgS in FeS at 1197 °C. At subsolidus temperatures, Skinner and Luce (1971) found no significant MgS dissolved in FeS, but vice versa, FeS dissolves readily in MgS.

To supplement the scarce information on the FeS-MgS system, the FeS-MnS system may be used as an analogue (Jantzen et al. 2017b). Due to its importance to the steel industry (Senuma 2002; Yan et al. 2019) the FeS-MnS system is well studied, also at temperatures higher than

1000 °C. A summary of the petrographic features of this system is found in Mann and Van Vlack (1976), who distinguish between a pyrrhotite and troilite (with excess Fe^0) system (see below).

FeS-CaS binary

Skinner and Luce (1971) found no detectable solubility of CaS in FeS and vice versa. Vogel and Heumann (1941) and Heumann (1942) studied the system above the eutectic temperature (≥ 1100 °C), but samples in their experiments underwent interaction with atmospheric O_2 and continuous sulfur loss. Sulfur loss was continuously counterbalanced by adding sulfur to running experiments. The formation of oxygen-bearing phases (e.g. SO_2) was reported (Heumann 1942). Despite these problems, the FeS-CaS eutectic was found to lie at 23.2 mol%, at 1120 °C (Vogel and Heumann 1941), later corrected to 14.3 mol% CaS, 1100 °C (Heumann 1942).

MgS-CaS binary

This system has been studied only at sub-solidus conditions, due to the high melting temperatures of both MgS and CaS of 2225 °C (Roine 2002) and 2525 °C (Juza and Bünten 1958). Skinner and Luce (1971) studied the binary solubilities of MgS and CaS in the temperature range between 600 and 1000 °C but did not report an experimental closure of the solvus. Primak et al. (1948) reported the reciprocal solubility based on X-Ray diffraction of a solution which carried a flux of NaCl at 1000–1100 °C.

FeS-MgS-CaS ternary

Skinner and Luce (1971) determined ternary subsolidus phase relations within the FeS-MgS-MnS-CaS system using microprobe analysis. Solid solutions in the ternaries of FeS-MnS-CaS and FeS-MgS-CaS were reported to be analogous, owing to the similar behaviour of MnS and MgS. In the FeS-MgS-CaS ternary, Skinner and Luce (1971) reported CaS to remain essentially binary toward MgS with very limited FeS dissolution (≤ 1 mol%) at 800 °C and up to 3 mol% FeS dissolved in oldhamite ss_{cub} at 900 °C. Based on their data, Skinner and Luce (1971) use the extent of solubility of FeS towards MgS and MnS to derive minimum temperatures of formation of enstatite chondrites. Oldhamite was found to be of no practical use as a geothermometer owing to the low Fe-solubility in its structure. Ternary studies above 1000 °C have not been conducted so far.

Similarity between MnS and MgS

It is noteworthy that MnS and MgS behave quite similarly in the sulfide systems, which manifests itself in the observation of oldhamite ss_{cub} coexisting with either Mg-rich or Mn-rich ss_{cub} (ninningerite or alabandite) in natural enstatite chondrites. Two coexisting MnS- and MgS-rich phases are ruled out due to a complete solubility in the MnS-MgS solid solution (Keil 1968). CaS forms a solvus with both MnS and MgS. The reason is likely in the similar lattice constants of cubic MgS and MnS (5.202 ± 0.0008 and 5.2234 ± 0.0008 Å, respectively) contrasting the one of CaS, which is 0.5 Å larger (5.6953 ± 0.0008 Å) (Skinner and Luce 1971). A review on how component volume mismatch affects the interplay of pure substances can be found in Davies and Navrotsky (1983).

To further constrain phase relations in these systems, we have performed experiments on FeS-MgS at 1170–1550 °C, on FeS-CaS at 1025–1600 °C, both on the melting loop; further on MgS-CaS at 900–1500 °C to better constrain the solvus between oldhamite and ninningerite solid solutions and in the ternary FeS-MgS-CaS between 1050 and 1360 °C, again on the melting loop. This data set in combination with literature data and estimates of pure endmember melting points are used to model solidus and liquidus relations thermodynamically.

Methodology

Experimental procedure

The starting sulfides were commercial FeS and CaS powders (99.99 wt% purity). MgS was synthesized at 500 °C for 24 h from Mg metal (99.8 wt% purity) and elemental S in graphite (C) capsules placed in evacuated and sealed silica glass tubes (5×0.8 cm). The absence of any detectable phase other than MgS was controlled using a *D8 Advance Bruker axis X-Ray Diffractometer*.

Pure substances were mixed in the required quantities, placed into graphite capsules, dried for two hours at 110 °C, and sealed into evacuated silica glass tubes (at 10^{-5} bar), providing a closed system with little oxygen. Nevertheless, gas pressure in the silica tubes built up during the experiments, and above 1300 °C, the silica glass softened and often expanded under the gas pressure, some glass tubes exploded above 1400 °C. This gas presumably consisted of S-bearing species (S_2 , H_2S , SO_2 etc.) and/or CO and SiO gas as reaction product of the silica glass tubes and graphite containers.

Sealed glass tubes were either heated in a *Nabertherm 1800 box furnace* (≤ 1350 °C) or in a GERO vertical tube furnace, where the evacuated glass tubes hung in a Pt wire-container, the uncertainty in temperature is ± 6 °C. At the

end of each experiment, the samples were manually moved or dropped into water to ensure rapid quench. Temperatures were measured using a B-type thermocouple located within 1–2 cm of the experimental charges. Run times ranged from 5 min to > 24 h depending on temperature (table *Runtimes*, supplementary material). Similar durations were used for lower temperature experiments for other sulfide systems (Skinner and Luce 1971). The sample-containing sealed glass tubes could hold up to 15 bars of internal gas pressure before exploding, however temperatures above ≈ 1300 °C lead to the glass tubes increasing their volume with time, resulting in lower internal pressures. Thus, our experiments were conducted in near atmospheric (1–15 atm) pressure, self-induced by the forming gas.

Samples were polished using water-free, oil-based polishing solution as especially oldhamite (CaS) is known to readily dissolve in water (Haberle et al. 2013; Zekker et al. 2011; Zvimba et al. 2011). Also, Ca-rich samples left in air for a while grew whiskers, reacting with ambient humidity, making it mandatory to work in low humidity environments and store samples in an inert environment. In our case, we prepared all samples in a 1 atm-pressure glove box maintaining < 3% relative humidity, built for this purpose.

Experimental strategy

The goal of studying troilite-bearing systems render it necessary to investigate a ternary sulfide-metal system and project the results into an inferred binary sulfide system. The necessary additional (non-sulfide) component, Fe^0 , stabilizes the stoichiometric troilite instead of the compositionally more variable pyrrhotite, which invariably forms in experiments lacking Fe^0 -saturation (shown for FeS-MnS by Mann and Van Vlack 1976). In our experimental setup, the unavoidable weak loss of sulfur via evaporation into the silica glass tube made it unnecessary to add Fe^0 to the experimental charges, however, shifted the experiment slightly towards a Fe^0 enriched composition relative to the stoichiometric binary. The consequence is that the Fe^0 content is minor, but sufficient to stabilize troilite rather than pyrrhotite. The stability of pyrrhotite results in phase relations (Mann and Van Vlack 1976) that differ from those we observe.

Analytical methods

Run products were characterized using optical and scanning electron microscopy (SEM, *JEOL JSM-6390*), and energy dispersive spectroscopy (EDS, *Thermo Noran NSS7*). Calibrated EDS analyses were conducted using a beam current around 20 nA and an acceleration voltage of 15 keV, standards are reported in table *EDS standards* (supplementary material). Analyses were performed in area scan mode (typically 30×30 μm). For thermodynamic modelling,

averages were mostly formed from samples with analytical totals > 96.5 wt%, however, at high temperatures and because of the difficult preparation of MgS and CaS (especially for quenched liquid), this was not always possible. We are aware that higher totals are preferable but due to the area scan mode that is required for non-quenchable phases and the wriggly surface quality of some of the studied phases, it was hard to obtain higher totals, mainly due to the presence of cracks and excessive voids. Average phase compositions within each experiment are from at least five area scans, thereby providing a test of the homogeneity throughout the charge. The thermodynamic evaluation of the data attributes a higher weight to textural evidence than to measured compositions (see “[Thermodynamic evaluation](#)”). At most temperatures, multiple experiments with the same textural features were obtained, then, averaged phase compositions of these runs were used for construction of phase diagrams.

Experimental results

The construction of phase diagrams requires textural interpretation of the experimental run products. This is because sulfide liquids do not quench to glasses devitrifying entirely into a variety of individual quench phases with textures that are highly dependent on liquid compositions and quench rates. Equilibrium solids at run temperatures are typically less affected by quench modification, and are thus straightforward to identify and measure compositionally. Therefore, the primary obstacle in deriving phase relations is to determine liquidus surfaces by identifying former liquids and their compositions. A priori constraints to determine the nature and number of former melt phase(s) come from the observed textures of quenched charges, but also from the phase rule. For example, in a binary system at any given temperature, a maximum of three phases can be observed at invariants points, but in the commonly observable divariant solid–liquid phase loops exactly two phases are stable in which case once one solid is identified, the remainder should represent a former melt.

Melt compositions of liquidus boundaries may either be directly measured by SEM–EDS through large area scans of former melts, or can be bracketed at a given temperature by investigating closely spaced starting compositions, observing the absence or presence of equilibrium solids solely on textural grounds. Both approaches are taken here, the textural evaluation is predominantly employed for the FeS–CaS system.

The setup of the experiments made any oxygen contamination in the sulfide phases minimal to such an extent, that in the experiments, no oxygen-containing phases were observed.

Solid phase textures

In the FeS–MgS and FeS–CaS systems, below the solidus, one solid solution and an almost pure FeS–solid phase are present. MgS ss_{cub} contains lamellae of almost pure FeS (Fig. 1a). In this system, lamellae orientations are useful to identify individual grain boundaries and sizes within the FeS-rich solid. In the FeS–CaS system, lamellae are absent. Individual grains are up to 300 μm in diameter often showing equilibrated $\sim 120^\circ$ triple junctions at grain boundaries.

Solid solutions surrounded by a liquid phase appear exclusively as near-spherical or rounded particles, lacking any sharp angular shapes (Fig. 1b, c). In some cases, equilibrium solids are modified during quench, as indicated by a gradual compositional zoning towards their rims (Fig. 1b). In the MgS–CaS system, solids are chemically homogenous in the investigated temperature range and have sizes $\geq 10 \mu\text{m}$. The ternary (Fig. 1c, d) does reproduce the same features as in the FeS–MgS and FeS–CaS binary systems.

Quenched liquid textures

Melts suffer from severe quench modification, which have characteristic features in each system.

Quenched liquids in the FeS–MgS system typically consist of small dendritic forms of an MgS-rich solid solution within almost pure FeS. In areas where there are no MgS exsolutions and that are farthest from MgS-containing solid solutions, exsolutions of Fe^0 ($< 1\text{--}2 \mu\text{m}$), surrounded by almost pure FeS are present (Figs. 1b, 2c), a result of the Fe^0 -excess that cannot be avoided when studying troilite. While the Fe-metal precipitates are micron-sized, the MgS-rich quench-features are about 20–30 μm . MgS exsolution features often show a long-range geometry with characteristic angles of branching dendritic arms.

Liquids in the FeS–CaS system exsolve small ($< 1 \mu\text{m}$) CaS-rich particles (Fig. 2a), which are arranged as larger spherical (cauliflower- or fan-like) structures. Within these fan-structures, no other quench phase is present. The CaS-rich exsolutions that make up these structures are again surrounded by pure FeS. Where darker CaS exsolutions are not present, Fe^0 may be found as exsolutions within pure FeS as veins or other angular shapes between the fan-structures.

Secondary electron images of the FeS–CaS system (Fig. 2b) reveal that the surfaces of CaS-rich exsolutions are often topologically depressed in comparison to the surrounding FeS-rich phases, indicating selective loss of the CaS component during sample preparation. Banning water from the polishing process improved the surface quality, but samples still showed some topography, indicating mechanical erosion of CaS. Therefore, measured CaS concentrations may be slightly underestimated, hence, liquidus boundaries are predominantly bracketed by using different starting

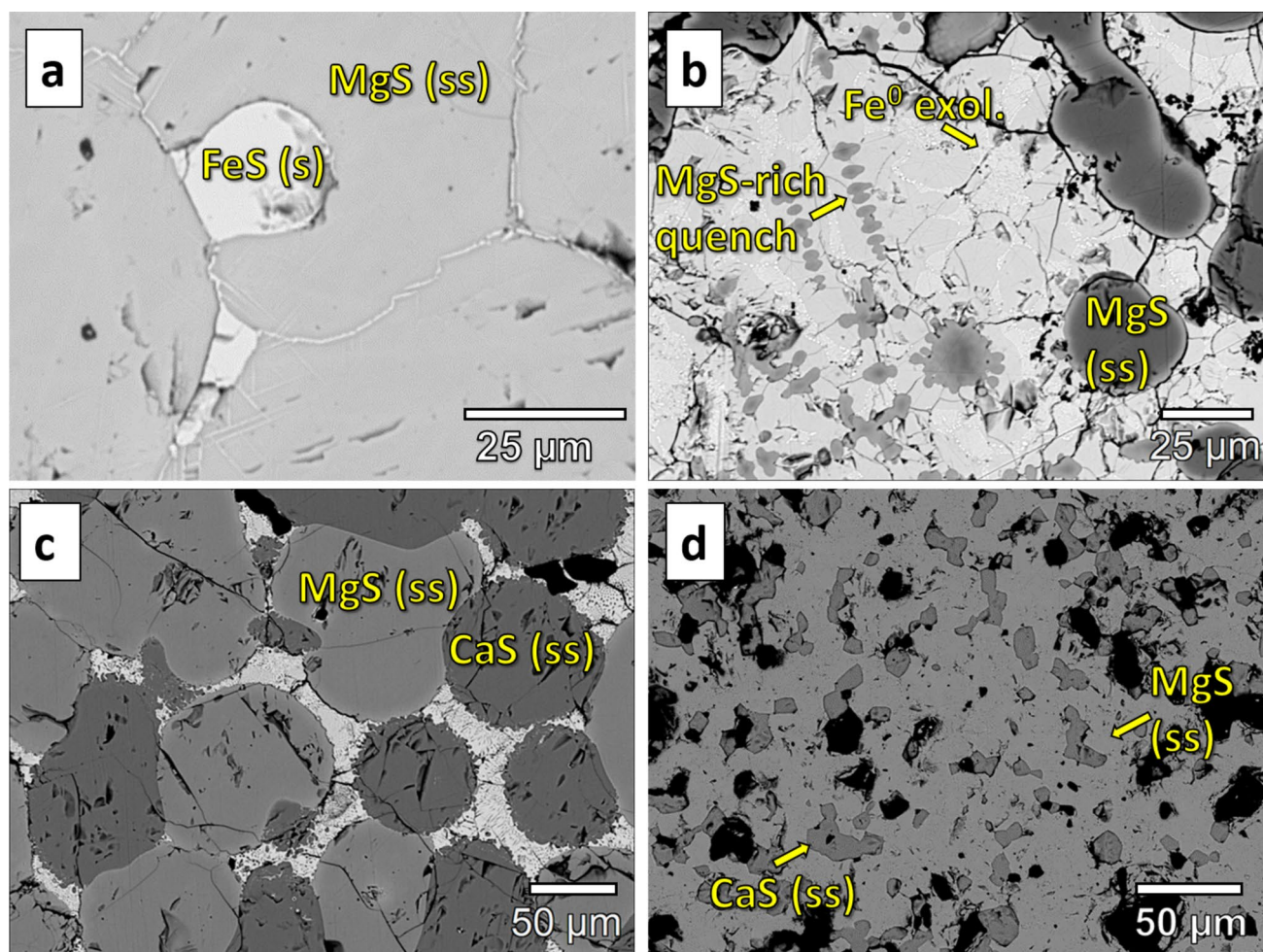


Fig. 1 Back-scattered electron (BSE) images of the typical appearance of solids in the FeS-MgS-CaS system. **a** Niningerite solid solution coexisting with troilite (s) below the eutectic temperature in the FeS-MgS binary system (tronic 34 – 1170 °C). **b** Niningerite solid solution in equilibrium with a quenched liquid phase, showing both MgS-rich exsolutions and Fe⁰ exsolutions (tronic 86–1400 °C). **c** Two

solid solutions coexisting with an interstitial quenched liquid phase in the FeS-MgS-CaS ternary (ter 20–1152 °C). **d** Two solid solutions of CaS ss_{cub} and MgS ss_{cub} at the absence of any liquid phase, also in the ternary system (ter 19–1152 °C). The black features in all images are plug-outs

compositions. Depending on the texture of the quenched liquid, the amount of CaS-loss is estimated to 2–10 mol%, the higher deviations expected at higher experimental temperatures (higher CaS-concentrations in the liquid), both for the FeS-CaS binary as well as for the ternary system. The CaS erosion effect was also observed for equilibrium solids but to a much lesser extent. From the direct textural difference of homogenous solid phases, compared to quenched liquids separated into multiple phases, the measurements for the solids remain unaffected by the preferential erosion effect of CaS phases.

Quenched liquids in the ternary system show combined features of the two binaries, such as fan-like CaS rich exsolutions and round FeS-blobs, which are cross-cut by MgS-rich dendrites. Fe metal in form of exsolutions occurs interspersed between both exsolution features but not in direct contact

with either CaS or MgS-rich exsolutions (Fig. 2c). Overall, liquid-rich run products tend to produce larger individual quench phases probably as a result of increased length scales over which exsolutions can grow (cf. Figure 1c vs. b and 2c).

The effects of excess iron

The observation of small Fe⁰-quench spherules interstitial to FeS-dominated quench (Figs. 1b, 2a, c), testifies for a metal-sulfur ratio in the melt that is slightly offset from unity, a feature that was also observed by Andreev et al. (2006). For both binary melt compositions, the ratio of measured cations (Mg, Ca, Fe)²⁺ and anions S²⁻ exhibits a 0–1 mol% S-deficit up to 1200 °C and up to 4 mol % at ≥ 1400 °C (tables FeS-CaS and FeS-MgS, supplementary material). Instead, to 1200 °C, the FeS-rich solids

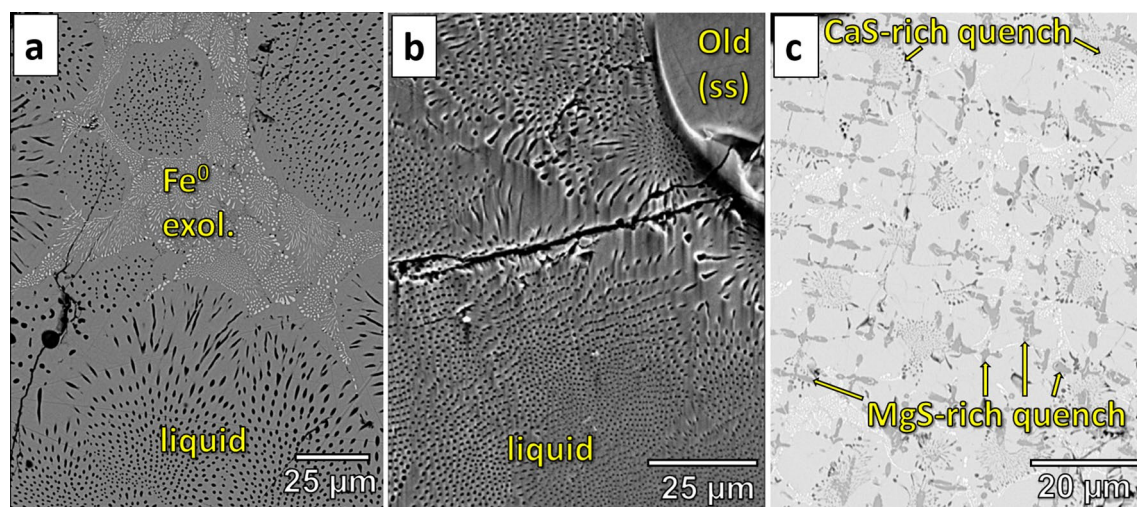


Fig. 2 Quench features in the liquid fraction: **a** BSE image of FeS-CaS liquid with CaS-rich quench features, arranged in a spherical “cauliflower” texture (CaS=black dots and stripes). Fe^0 exsolutions (small, bright white dots) are in between cauliflower textured areas (troold 97–1136 °C). **b** The typical surface topography of a FeS-CaS sample (secondary-electron surface imaging). Small quench phases, high in CaS within the liquid phase are (partially) lost probably due

to a mechanic effect during polishing prior to analysis. (troold 102–1136 °C); **c** BSE image of MgS and CaS quench features typically found in liquid-rich experiments in the ternary. Whereas CaS produces small exsolutions in fan-structures, MgS forms an arrangement resembling a dendritic and repetitive angular pattern (indicated by arrows), which may crosscut other exsolution features, such as CaS and Fe^0 exsolutions (ter 58–1300 °C)

are comparable to natural troilite stoichiometry (Carpenter and Desborough 1964) and $\text{MgS ss}_{\text{cub}}$ and $\text{CaS ss}_{\text{cub}}$ are stoichiometric within error at all investigated temperatures. Sulfur deficiency thus appears to be limited to FeS-rich liquids. Metallic Fe was not observed in direct contact with the solid phases, but was concentrated in the centre of quenched FeS-rich liquid. Moreover, where CaS exsolutions occur, Fe^0 exsolutions are absent in the quenched liquid (Fig. 2a, c).

All experiments started with monosulfidic mixtures in a closed system. The experimental results should thus ideally depict binary systems, assuming that carbon from the capsule remains inert. However, a small fraction of sulfur evaporates forming a gas in the evacuated glass-tubes, which is verified by the yellowish coloration on the inside of the glass tubes observed after quench. As a consequence, the solid + liquid portion of the stoichiometric starting composition is shifted towards slightly higher Fe:S ratios. The net effect is the formation of Fe^0 -quench precipitate, which in turn stabilises troilite but transforms the binary into ternary systems and the ternary into a quaternary (Fe-FeS-MeS; Me=Mg,Ca). However, because the very minor Fe^0 is dissolved in the sulfide melt, it has a negligible effect on phase relations, results of the experiments are still viable for determining the phase relationships of the FeS-MgS and FeS-CaS binary systems. The MgS-CaS binary system did not show evidence for Fe^0 precipitation and effectively represents a true binary. Concluding, the reported experiments yield troilite instead of pyrrhotite because of the Fe^0 component

dissolved in the sulfide liquid, the experiments are then as close as possible to a monosulfidic stoichiometry.

The FeS-MgS phase diagram

The system FeS-MgS was investigated at 1170–1550 °C, unfortunately, all evacuated silica glass tubes run at higher temperatures exploded. In total, 67 samples were run, the conditions of which are summarized in supplementary table “FeS-MgS” together with their textural interpretations. The results constrain subsolidus phase relations, the divariant melt loop, and the super-liquidus field, where melt compositions are within error identical to starting compositions in large-area scans of $\geq 150 \mu\text{m}$ diameter (e.g. experiment tronin 43 or 59, supplementary material). Measured and experimental starting compositions, coded for textures are shown in Fig. 3.

At temperatures ≤ 1190 °C, no liquid was found. Solid grains are typically 40–80 μm and consist of almost pure FeS and a niningerite solid solution with about 28 mol% MgS. At 1194 °C liquid was observed for starting compositions with < 40 mol% MgS. At higher MgS contents a one-phase region of $\text{MgS ss}_{\text{cub}}$ exists. The experiments suggest an invariant point near pure FeS at 2.5 ± 1 mol% MgS, with a temperature of 1192 ± 6 °C. Unfortunately, both melting temperature and composition of the invariant point are very close to those of pure FeS (1192 °C), and the uncertainty in our experimental temperature (± 6 °C) is above the accuracy needed to differentiate between a eutectic or peritectic

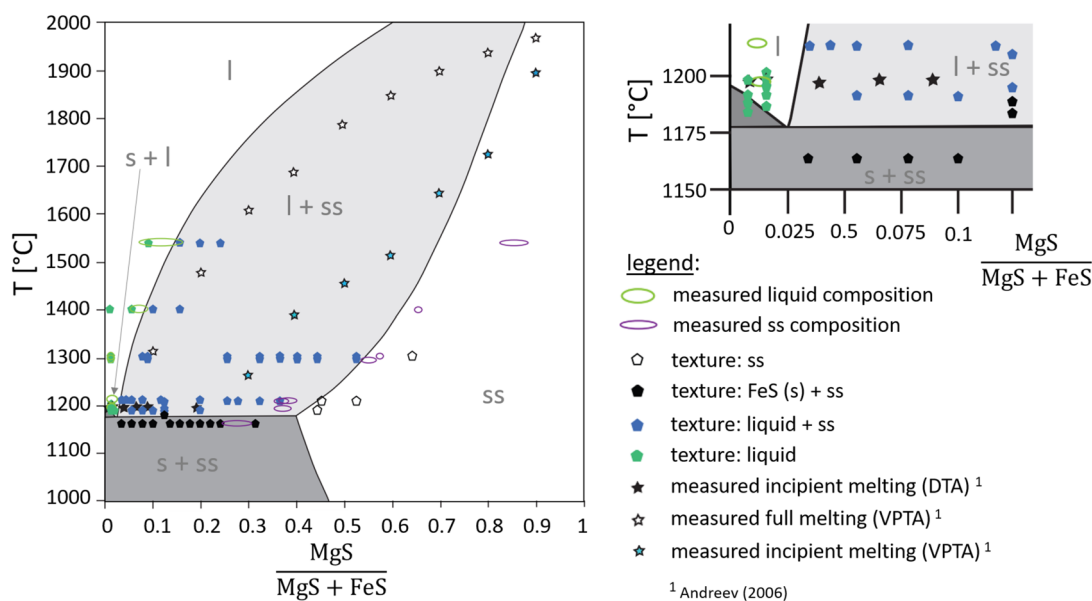


Fig. 3 The FeS-MgS phase diagram with experimental data and calculated phase boundaries. Previous data (stars) from Andreev et al. (2006) are from visual polythermal analysis are plotted for comparison.

system, leaving some uncertainty to the exact nature of this invariant point.

Measured FeS contents in the niningerite solid solution coexisting with liquid decrease strongly over the investigated temperature range, MgS contents increasing from 28.2 ± 2.7 mol% at 1170 °C to 84.0 ± 4.9 mol% at 1550 °C (purple ovals on Fig. 3). Over the investigated temperature range, the liquids in equilibrium with niningerite (green ovals in Fig. 3) exhibit a quite limited range of MgS contents reaching at most 12 mol% at 1550 °C, which implies an initially steep liquidus surface.

Repeat experiments in a vertical tube furnace at 1170 °C and 1300 °C yield results identical within error (supplementary material). Employing both the box furnace for a first series and the vertical tube (drop quench) furnace for a second series at 1200 and 1300 °C, again the same results were obtained, underlining their robustness.

The FeS-CaS phase diagram

The system FeS-CaS was examined in the temperature range 1025–1600 °C. The 159 individual experiments are listed in table “FeS-CaS” in the supplementary material. As for the FeS-MgS systems, experimental observations cover subsolidus, divariant solid–liquid and pure liquid fields. The location of liquidus surfaces is mostly determined by bracketing through closely spaced starting compositions, rather than direct liquid measurements.

At temperatures lower than 1063 °C, Fe⁰ exsolutions were absent and no liquid was found, indicating a subsolidus

son. Depicted phase boundaries were computed from a thermodynamic model that was fit to the experimental data (“Thermodynamic evaluation”). ss = solid solution

assemblage. For temperatures higher than 1063 °C, textures indicative of melt with either pure solid FeS or CaS ss_{cub} have been found across the different starting compositions, indicating eutectic behaviour. The eutectic temperature has been bracketed between 1060 and 1067 °C (troold 28–troold 55), i.e. 1063 ± 3 °C, with a eutectic composition of 7 ± 1 mol% CaS, which compares to the 1100–1120 °C and 14–23 mol% by (Vogel and Heumann 1941) and (Heumann 1942), experimenting in open systems.

The reproducibility of the solid solution compositions was generally excellent with 2σ standard deviations below 1 mol% between individual experiments at the same experimental temperature. The 1133 °C series was repeated at 1136 °C, yielding measured compositions of the CaS ss_{cub} within error range of the dataset at 1133 °C. Instead, measured liquid compositions show a larger variability of up to ± 7 mol% in a given experiment and are reported in the supplement.

The MgS-CaS phase diagram

The absence of experimental phase equilibrium data on the melting loop stems from its temperatures of > 2100 °C. Our data essentially texturally verify the previous experimental constraints of Skinner and Luce (1971), which is used for modelling and are displayed in table “MgS-CaS” in the supplementary material. Our own data contribute with two points (1350 °C and 1500 °C) to the modelling, adding constraints on the closure of the solvus. Texturally, our own experiments are consistent with those of Skinner and Luce

(1971) (Fig. 5) but not with Primak et al. (1948), who determined compositions from unit cell measurements.

The FeS-MgS-CaS ternary system

The ternary system was studied at six temperatures (1050–1360 °C). The experimental results are presented in Fig. 6, liquid was observed at temperatures ≥ 1100 °C. The liquid is present as small quench-exsolutions of > 2 μm in a matrix of quenched FeS (strongly resembling the FeS-CaS binary system on the FeS side), with up to 2 mol% MgS dissolved in the quenched liquid. The Ca-rich exsolutions were hard to preserve during preparation and polishing and hence measured compositions of the liquid phase may be slightly CaS-deficient. The effect of Ca-deficiency was found to be less in the ternary than in the FeS-CaS binary, probably due to smaller exsolution features compared to the binary system.

A three-phase field exists between the experimental temperatures 1050 °C and 1240 °C, where a FeS-rich melt (liquid $> 1063 \pm 3$ °C $<$ FeS (s)), coexists with two distinct solid solutions, one rich in CaS and low in both MgS and FeS, and one with varying amounts of FeS, MgS and CaS, where the Ca and Mg contents increase with temperature (Fig. 6b, c). Note, that experimental data for 1240 °C are projected onto the 1250 °C model (Fig. 6d).

Thermodynamic evaluation

Model and parameters

We invert the experimental data to parameterize thermodynamic solution models for the ss_{cub} and liquid phases under the assumption that the solubility of Mg and Ca in troilite is insignificant. The unknown molar Gibbs energy of the hypothetical cubic FeS endmember, f, is expressed

$$g_{\text{f}} = g_{\text{tro}} + a_{\text{f}} + b_{\text{f}}T \quad (1)$$

where a_{f} and b_{f} are among the unknown parameters to be determined by the inversion, T is the temperature in Kelvin, and g_{tro} is the Gibbs energy of pure troilite at the temperature of interest and ambient pressure. The molar Gibbs energy of troilite and all other pure endmembers are computed as

$$g = g^0 - \int_{298}^T \left(s^0 + \int_{298}^T \frac{c_p}{T} dT \right) dT \quad (2)$$

where g^0 and s^0 are, respectively, the molar Gibbs energy and entropy of the endmember at 298 K, and c_p is a polynomial

$$c_p = c_1 + c_2T + \frac{c_3}{T} + c_4T^2 \quad (3)$$

representing its isobaric molar heat capacity. The thermodynamic data for these endmembers (Table 1) are taken from Roine (2002), with the modification that the heat capacity of pure solids is taken to be constant beyond the melting point of the solid. Additionally, the heat capacity data provided here for troilite is valid only in the temperature range 598–1465 K, accordingly g_{tro}^0 and s_{tro}^0 are extrapolations that reproduce the true properties of troilite only at $T > 598$ K.

The molar Gibbs energy of the liquid and ss_{cub} are expressed as:

$$g = \sum_{i=1}^c y_i g_i + RT \sum_{i=1}^c y_i \ln y_i + g^{\text{excess}} \quad (4)$$

where R is the universal gas constant, y_i is the mole fraction of endmember i , c is the number of endmembers, and g^{excess} is an excess function consisting of second and third order interaction terms of the general form

$$g^{\text{excess}} = w_{ij}y_iy_j + \dots + w_{ijk}y_iy_jy_k + \dots + w_{ijk}y_iy_jy_k. \quad (5)$$

Table 1 Thermodynamic data (Eqs. 2 & 3) used for estimating FeS-MgS-CaS ss_{cub} and liquid models

Endmember	T_m , K	g^0 , kJ/mol	s^0 , J/mol/K	c_p , J/mol/K			
				c_1	c_2	c_3	c_4
Oldhamite, CaS	2798.15	−499.260	56.500	46.291	0.00837	−118,800	
Troilite, FeS	1465.15	−116.686	66.251	94.584	−0.08366	141,000	4.79E-05
Niningerite, MgS	2498.15	−360.705	50.330	45.544	0.00876	−230,700	
CaS-liquid		−448.661	55.394	67.000			
FeS-liquid		−90.343	91.859	62.551			
MgS-liquid		−317.931	47.907	67.000			

T_m : melting point of the solid endmembers. Data, which is not indicated by an index is taken from Roine (2002),: a: measured via X-Ray high-temperature monitoring of the changes of lattice sizes with temperature in a CaS-CaC₂ system (Juza and Bünzen 1958). b: Higher end of the range of experimentally derived melting temperatures in the literature (between 2000 (Andreev et al. 2006) and 2225 °C (Roine 2002)). Troilite is not a ss_{cub} endmember itself; however, the molar Gibbs energy of the hypothetical cubic FeS endmember for modelling is expressed relative to that of troilite (Eq. 1)

The interaction coefficients $w_{...}$ in Eq. 5 are allowed a linear temperature dependence such that

$$w_{...} = a_{...} + b_{...}T. \quad (6)$$

The number and nature of the terms in Eq. 5, and the values of the coefficients in Eq. 6, are the remaining unknowns to be determined by inversion.

Parameter inversion

We employ a Monte Carlo inversion strategy similar to that described by Khan et al. (2021) that is implemented by the program MC_fit within the Perple_X Gibbs energy minimization software (release 7.1.5, Connolly, 2009). The strategy consists of randomly enumerating starting guesses for all unknown parameters within specified ranges. These ranges do not limit the final result but do bias results towards values within the specified range. For each guessed parameter set, the Melder-Nead algorithm is used to find a set of parameter values that minimize an objective function that characterizes the difference between the experimentally observed phase equilibria and that predicted from the parameters by Gibbs energy minimization at the conditions of the individual experiments. The best fit parameters are identified as those which yield the lowest value of the objective function. The objective function is the sum of scores for the individual experiments. In turn, the scores for observation i are the sum of three terms f_i^{pred} , f_i^{extra} , and f_i^{comp} that account for: the number of observed phases correctly predicted, m^{pred} ; the number of phases predicted but not observed, m^{extra} ; and the discrepancy between the compositions of the observed and correctly predicted phases. Specifically, the terms are

$$f_i^{\text{pred}} = W^{\text{pred}}(1 - m^{\text{pred}}/m^{\text{obs}})^2 \quad (7)$$

$$f_i^{\text{extra}} = W^{\text{extra}} \left(\sum_{j=1}^{m^{\text{extra}}} (x_j) \right)^2 \quad (8)$$

$$f_i^{\text{comp}} = \sum_{j=1}^{m^{\text{pred}}} \left(\sum_{k=1}^c (y_{jk}^{\text{obs}} - y_{jk}^{\text{pred}})^2 \right) \quad (9)$$

where m^{obs} is the number of phases observed, x_j the predicted mass fraction of extraneous phase j , y_{jk}^{obs} and y_{jk}^{pred} are the mole fractions of endmember k in, respectively, the observed and predicted phase j , and W^{pred} and W^{extra} are arbitrarily specified weighting factors. The scoring differs from that of Khan et al. (2021) in that f_i^{pred} has been made quadratic and that f_i^{pred} has been made proportional to the phase fraction. The latter adjustment reduces the penalty for predictions of

small amounts of phases that might be difficult to observe experimentally. The weights W^{pred} and W^{extra} are set to 10 to magnify the penalty for failing to predict an observed phase and for predicting a phase that is not observed relative to penalty for mismatch between the compositions of observed and correctly predicted phase.

To derive an excess function (Eqs. 5 & 6) parameterization of minimal complexity we adopted a piecewise approach to the inversion in which we sequentially inverted for the unknown parameters pertinent to the FeS-MgS binary, the FeS-CaS binary, and the ternary experiments.

FeS-MgS: The FeS-MgS binary is our densest dataset. This data was augmented by a pseudo-data point at 1190 °C to assure that troilite is predicted as the stable, pure FeS, condensed phase at temperatures below the liquidus. The parameters estimated from this dataset were the molar Gibbs energy of the hypothetical cubic FeS endmember (Eq. 1; Table 2) and the liquid and ss_{cub} FeS-MgS interaction coefficients. The dataset is well-represented by simple regular solution models (w_{fm}^{l} and w_{fm}^{s} in Eq. 5; Table 2), which fit 67 out of 67 observations. The signs on the hypothetical cubic FeS endmember parameters a_{f} , and b_{f} , are consistent with the expectation that the high-symmetry cubic FeS endmember is more disordered than troilite and therefore becomes less metastable with respect to troilite with increasing temperature.

FeS-CaS: Given the estimate of the molar Gibbs energy of the cubic FeS endmember obtained from the FeS-MgS binary analysis, the unknowns to be derived from the FeS-CaS dataset are the FeS-CaS binary interaction term for liquid and ss_{cub} . Although a regular interaction term (w_{fc}^{s}) is adequate to describe ss_{cub} , it emerges that the skewed eutectic in this system cannot be reproduced without introducing third order interaction terms ($w_{\text{fcc}}^{\text{l}}$, $w_{\text{ffc}}^{\text{l}}$, Eq. 5) for

Table 2 FeS-MgS-CaS liquid and ss_{cub} model parameters (Eq. 6) derived by inversion of experimental data

Parameter	a , kJ/mol	b , J/mol/K
g_{f}^{s}	5.89917	−0.612554
w_{fm}^{s}	7.0244	
w_{fc}^{s}	31.5850	
w_{mc}^{s}	47.0081	−14.3522
$w_{\text{fmc}}^{\text{s}}$	117.077	−77.053
w_{fm}^{l}	9.44929	
$w_{\text{fcc}}^{\text{l}}$	741.342	−332.453
$w_{\text{ffc}}^{\text{l}}$	65.1274	−96.4949
w_{mc}^{l}	74.5217	−24.6964
$w_{\text{fmc}}^{\text{l}}$	24.9325	−76.3245

Superscripts l and s refer to liquid and ss_{cub} phases; subscripts f, m, and c denote FeS, MgS, and CaS endmembers of the liquid or solid phase

the liquid. If the liquid interaction coefficients are taken to be constants, then FeS–CaS liquid immiscibility is inescapable at high temperature. While our experimental observations do not preclude such behavior, we consider it unlikely. Accordingly, we ascribe a temperature-dependence to the interaction coefficients for the liquid phase (Eq. 6, Table 2), which is consistent with the expectation that increasing temperature favors ideal solution behavior. The resulting model successfully predicts 118 out of 122 observations (the exceptions being the experiments troold 32, 37, 95, 105).

FeS–MgS–CaS: Data for the ternary inversion were augmented by low-temperature (700–1000 °C) experimental data on the MgS–CaS ss_{cub} solvus from Skinner and Luce (1971). Given the previously estimated binary interaction coefficients, the unknowns to be derived from the FeS–MgS–CaS dataset are the MgS–CaS binary and FeS–MgS–CaS ternary interaction terms. The experimental observations were found to be adequately represented (Figs. 5 and 6b–e) by regular terms for both ss_{cub} (w_{mc}^s, w_{fmc}^s) and the liquid (w_{mc}^l, w_{fmc}^l ; Table 2). The resulting model successfully predicts 61 out of 62 observations, the exception being an experiment at 1000 °C from Skinner and Luce (1971).

Discussion

FeS–MgS

Our experiments (tronin 99–109; supplementary material, table FeS–MgS) show that there is an invariant point located close to FeS in both composition and melting temperature. To distinguish between a previously proposed eutectic (Dilner et al. 2016) or peritectic (Andreev et al. 2006; Jantzen et al. 2017b), was unfortunately not possible due to both a relatively large uncertainty of the exact melting point of troilite as a result of its variable chemistry (Fleet 2006) and due to the experimental uncertainty in temperature (± 6 °C).

The optimized thermodynamic model (Table 2) matches the experimentally determined phase boundary well (Fig. 3). In order to keep our model as simple as possible, we modelled a eutectic system following Dilner et al. (2016), but cannot explicitly rule out a peritectic topology. The modelled eutectic temperature of 1180 °C fits well to our experimental observations of the onset of melting between 1190 and 1194 °C ± 4 °C. A closer distinction between the higher or lower bound of this experimentally determined temperature range would make the difference between a eutectic and a peritectic system, which according to Andreev et al. (2006) lies at 1197 °C at 2 mol% MgS. The calculated Fe^0 -saturated phase diagram of Jantzen et al. (2017b), based on previous data (Andreev et al. 2006; Skinner and Luce 1971), resulted in a peritectic system at the melting point of troilite at 2 mol% MgS for the invariant point and 75 mol% FeS

for the maximum concentration in MgS ss_{cub} . The modelled melting temperature of MgS is inconsistent with Andreev et al. (2006), who estimated MgS melting to 2000 °C, while Jantzen et al. (2017b) modelled this system with 2240 °C as MgS melting temperature. Our steeper liquidus and solidus curves compared to Andreev et al. (2006) match well with ≈ 2240 °C for the melting of MgS, but not with 2000 °C. A direct determination of especially the melting point of MgS would be beneficial to eliminate persisting uncertainty in the FeS–MgS binary system, which however, is highly challenging. Our own attempts failed due to pre-melting partial evaporation and various reactions of pure MgS.

The observed differences between this study and Andreev et al. (2006) and also between our model and previous ones (Dilner et al. 2016; Jantzen et al. 2017a, b) may be reconciled by the observations of Mann and Van Vlack (1976) who noted that, in the MnS–FeS system, an Fe^0 -excess leads to troilite as the dominant form of FeS, while Fe-deficient systems stabilise pyrrhotite.

The invariant point of pyrrhotite_{s.s.} depends on the amount of iron and can be lowered to 1091 °C (Mann and Van Vlack 1976; Sharma and Chang 1979; Walder and Pelton 2005). The modelled melting point of pure FeS is much higher (1192 °C) (Moreau et al. 2022; Roine 2002; Taylor 1970). As a consequence of our study, where FeS–MeS (Me = Ca, Mg) are in equilibrium with Fe^0 in very low amounts (~ 1 – 2 mol%), the reported invariant points represent p1 in Fig. 4 of Mann and Van Vlack (1976), which can be used to project the binary phase relations of the sulfide-only assemblage. Andreev et al. (2006) used both FeS with an excess of S ($FeS_{1.03}$ was used as starting material for the FeS phase) thus suppressing a Fe^0 phase, and stoichiometric FeS. They only report one phase diagram for the FeS–MgS system and do neither detail which bulk composition (stoichiometric FeS or $FeS_{1.03}$) was used for construction, nor report Fe:S ratios in the observed phases. Their FeS phase thus probably represents a pyrrhotitic modification, while our study is closer to stoichiometric FeS and the FeS–MnS system of Mann and Van Vlack (1976). In summary, the difference between our and Andreev et al. (2006)'s phase diagrams is best attributed to troilite ($FeS\text{--}MgS \pm Fe^0$) in our study and pyrrhotite ($Fe_{1-x}S\text{--}MgS$) in Andreev et al. (2006).

FeS–CaS

In accordance with previous experimental studies, the FeS–CaS system has been found to be eutectic in nature with the invariant point at 1063 ± 3 °C and 7 ± 1 mol% CaS. This compares to the revised eutectic of Heumann (1942) at 1100 °C, 14.3 mol% CaS, which then led to modelled values of 1051 °C, 10 mol% CaS (Jantzen et al. 2017b) or 1030 °C, 14.3 mol% CaS (Dilner et al. 2016). As our study is the only experimental one that had modern analytical facilities

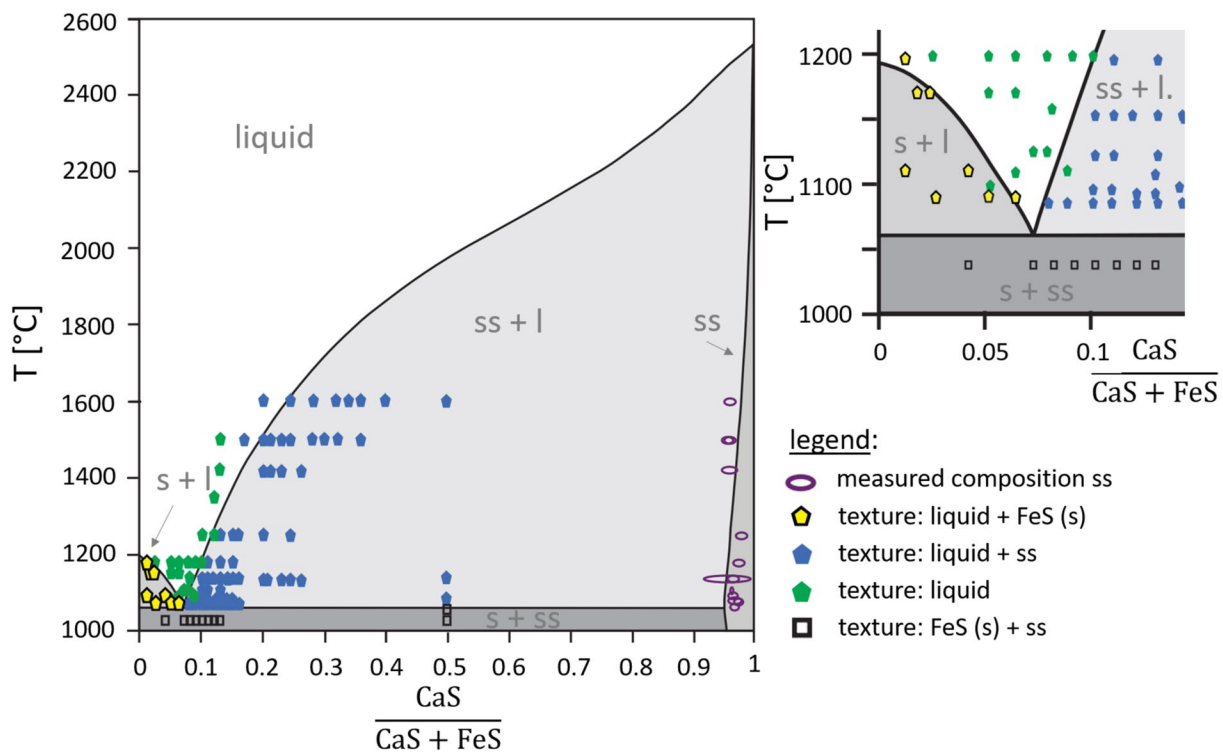
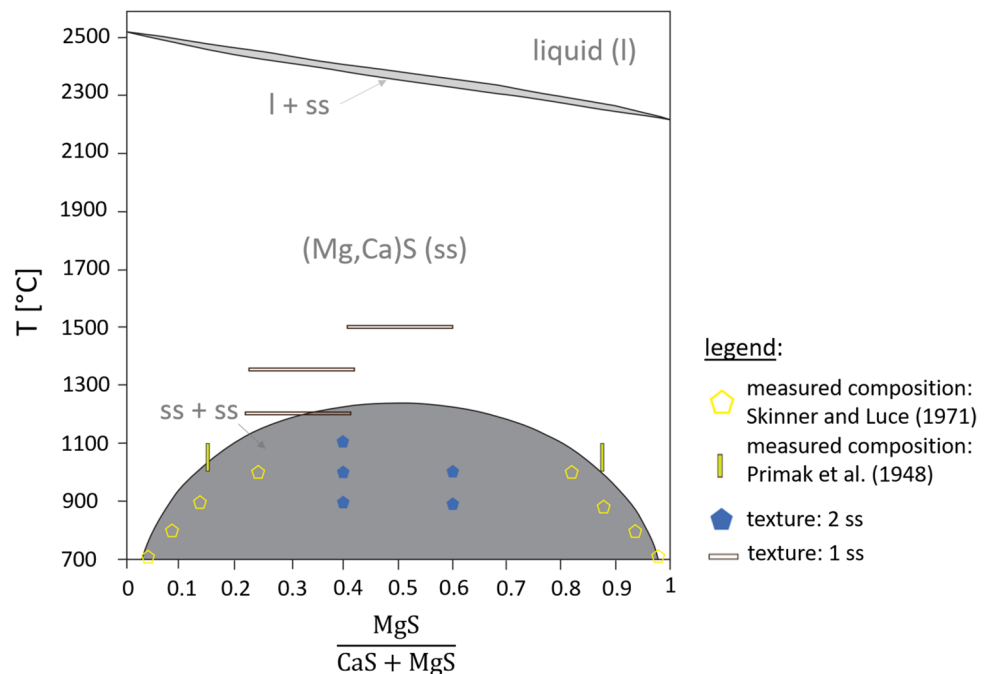


Fig. 4 The FeS-CaS phase diagram with relevant data. The system has a eutectic at 1063 ± 3 °C and 7 ± 1 mol% CaS. Phase boundaries were computed using the thermodynamic model derived in “[Thermodynamic evaluation](#)” from the experimental data

Fig. 5 Modelled MgS-CaS binary phase diagram. Depicted phase boundaries were computed from the thermodynamic model described in “[Thermodynamic evaluation](#)”. Depicted textural data was only used to verify the previously reported experimental observations and to set an upper temperature limit on the modelled solvus (at 1350 °C and 1500 °C). The rest of our own data was used only as a secondary validation, not contributing to the modelling part. One phase experiments are indicated by a bar, showcasing the compositional spread between starting composition (known) and measured composition, which however is known to be a false number due to considerable problems with the measuring instrument



at hand, did not suffer from interaction with oxygen, and our measured melt compositions agree well with phase saturation as a function of bulk composition, we believe that our values are accurate.

The extent of CaS ss_{cub} has been found to be limited to < 1 mol% FeS at 1000 °C (Skinner and Luce 1971). Heumann (1942) found approximately 2.6 mol% solubility of FeS in oldhamite at 1100 °C, which is consistent with our

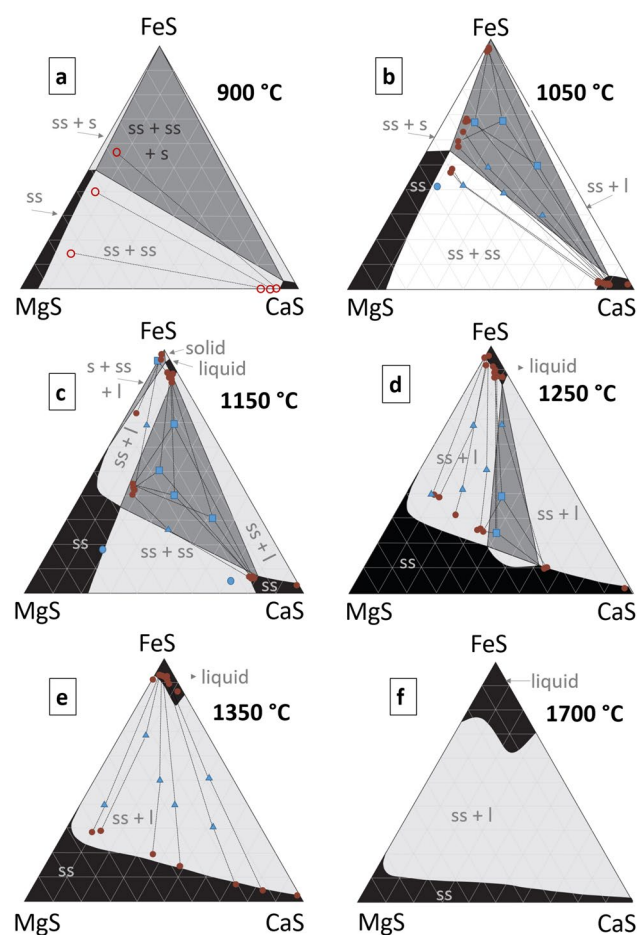


Fig. 6 Experimental results and modelled isothermal sections of the ternary phase diagram FeS-MgS-CaS in mol%. The results of experiments at 1050 °C, 1150 °C, 1240 °C, 1360 °C are placed in the closest temperature plot (b-d respectively). Blue symbols are starting compositions connected by lines to the (brown) measured phase compositions of an experiment; Triangles signify 2-phase assemblages; squares 3-phase assemblages; Blue circles indicate starting compositions that did not separate into multiple phases and lie in one phase field. Data points at 900 °C (a) are from Skinner and Luce (1971) who do not report starting compositions. Depicted phase boundaries were computed from a thermodynamic model that was fit to the experimental data (“Thermodynamic evaluation”)

study yielding a maximum of 3 ± 1.5 mol% at temperatures below the eutectic temperature and 1025 °C.

The textures and hence interpretation of the liquidus loop in this work diverge from those reported by Vogel and Heumann (1941), who interpreted dendritic CaS as equilibrium growth. The texture of solid CaS in our study, i.e. large homogeneous crystals, indicates equilibrium phases. The previous potentially erroneous interpretation of experimental textures (Heumann 1942; Vogel and Heumann 1941) may provide one explanation for the difference in the observed eutectic composition and temperature. Further, Heumann (1942) and Vogel and Heumann (1941) report an overabundance of sulfur, but no information on

the FeS stoichiometry is available. Due to the open system character of their experiments, Heumann and co-workers counterbalanced the observed S loss by adding S and report vigorous reactions when CaS was added to an $\text{FeS} \pm \text{S}$ melt (Vogel and Heumann 1941). Likely, the result of Heumann and co-workers was influenced by non-stoichiometry. The Fe-S binary calculated by FactSage 8.2 (Bale et al. 2009) predicts a slightly higher melting temperature for pyrrhotite of $\text{Fe}_{(0.96)}\text{S}$ composition than for troilite. This pyrrhotitic composition may still be high enough in Fe to assume a hexagonal structure (Thomas et al. 2003) and could modify the pseudobinary phase diagram (Mann and Van Vlack 1976). Our system was on the pseudobinary, produced a troilite FeS phase and yielded euhedral textures of the solid phases.

MgS-CaS

Unfortunately, our own attempts to verify the existing solvus data (Primak et al. 1948; Skinner and Luce 1971; Vogel and Heumann 1941) were hampered by a probable not-fully equilibrated state of the samples at temperatures ≤ 1000 °C. Our textural results clearly support the data by Skinner and Luce (1971) and contradict higher solubilities at higher temperatures, as indicated by Primak et al. (1948). Textural evidence ≥ 1100 °C was also used to limit the extent of the solvus in this system. We still found evidence at 1100 °C for the coexistence of two phases.

As there are no experimental data on the melting loop, we evaluated interaction parameters for this system together with ternary evidence at higher temperatures. While a temperature dependence was necessary for these interaction parameters, we decided to implement a symmetric model for simplicity. This is contrary to previous models (Dilner et al. 2016; Jantzen et al. 2017b), which used an asymmetric approach for the solvus. We, however, do not find the experimental evidence for an asymmetric solvus conclusive, and thus retained the simplest solution. We report a modelled closure of the solvus at 1210 °C, which is about 100 °C higher than modelled by Jantzen et al. (2017b). As a consequence of our choice to keep the model simple, our symmetric solvus slightly underestimates MgS concentrations (4 mol% at 1000 °C) in CaS ss_{cub} as well as MgS concentrations in MgS ss_{cub} . Considering our own additional textural evidence to the data of the previous study, and the choice to keep the model simple, we find our own model agrees reasonably well with pre-existing data (Fig. 5).

The liquid interaction parameter has been modelled as a part of the ternary system and thus produces a projected liquidus, which is not verified by binary experimental data. Considering the high temperatures that are necessary to achieve direct binary evidence however, a better solution is unfortunately not possible with the means applied here.

FeS-MgS-CaS

To our knowledge, the sole available ternary data have been collected by Skinner and Luce (1971) for subsolidus temperatures at 700, 800 and 900 °C for a quite limited amount of compositions. Reporting two experiments at 700 °C and three for both 800 and 900 °C, the likely extent of both the three-phase field as well as the two-phase field of the MgS- and CaS-rich solid solutions (coexistent with almost pure FeS) were roughly mapped out, however not used to derive a model. Their observations do generally match both the phase observations as well as the model result at 900 °C (Fig. 6a).

Our model predicts solubilities of MgS in CaS and vice versa (at 900 °C) that are lower, 6 mol% MgS in this study, compared to 11.5 ± 1.5 mol% MgS in Skinner and Luce (1971). Solubilities as high as those reported in Skinner and Luce (1971) (i.e. 15 mol% CaS in MgS ss_{cub}) are predicted to occur at much higher temperatures (ca. 1050 °C). The solidus surface (Fig. 7b) is defined by the relatively constant and low solubility of FeS on the oldhamite or Ca side and a highly variable FeS-solubility on the niningerite or Mg-side. Up to a modelled temperature of 1258 °C, a liquid plus two solids 3-phase field is defined by the distinct compositions of oldhamite and niningerite ss_{cub} . These two coexisting solid solutions (Fig. 1a) at ≤ 1258 °C are the result of the solvus in

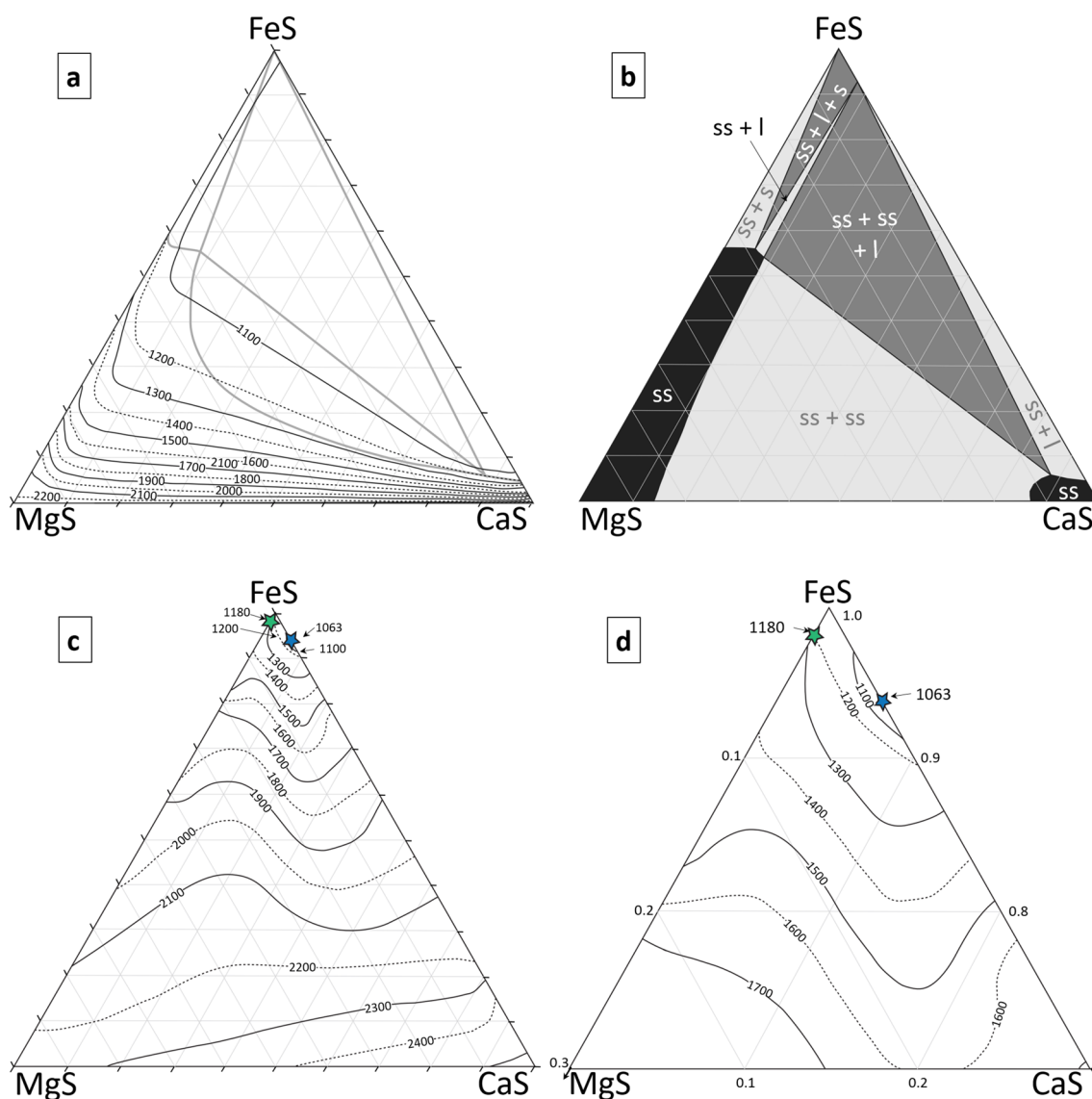


Fig. 7 **a** Solidus temperature contours of the ternary system FeS-MgS-CaS in °C. **b** Isothermal section at 1063 °C ($\geq$ eutectic temperature). **c** Liquidus temperature contours of the ternary system FeS-

MgS-CaS in °C with modelled eutectic points (stars) of the FeS-MgS (green) and FeS-CaS (blue) binaries. **d**: Close-up of the ternary system for FeS-rich compositions

the MgS–CaS binary system, which extends into the ternary. Higher temperatures ($> 1258\text{ }^{\circ}\text{C}$) lead to a phase that exhibits solid solution across the MgS–CaS join with fractions of FeS that reach up to 40 mol % on the MgS-rich side but only to 5 mol % on the CaS-rich side.

Liquid–solid two phase regions exist as either liquid—MgS ss_{cub} (for bulk compositions roughly equal in FeS, MgS, and CaS) or as liquid—CaS ss_{cub} (for starting compositions high in CaS relative to MgS).

The first liquid appears in the ternary at $1063 \pm 3\text{ }^{\circ}\text{C}$, factually in the FeS–CaS eutectic as it does not incorporate MgS. Higher temperatures lead to the expansion of this liquid field towards both higher and lower amounts of CaS at higher MgS mole fractions. Close to the melting point of FeS ($1192\text{ }^{\circ}\text{C}$), the FeS–MgS binary side is truncated by the expansion of the liquid surface. Higher temperatures now lead to an expansion of the liquid field towards higher MgS and CaS compositions. Compositions that are roughly equal in MgS and CaS do show a higher solid solution stability, translating to a concave liquidus surface (Figs. 7c & d).

Please note that our model does not reproduce the exact compositions for MgS ss_{cub} in the temperature range between 1100 and $1300\text{ }^{\circ}\text{C}$ (Fig. 6c and d), predicting lower FeS concentrations than experimentally indicated. While the pure FeS–MgS system does in fact model the experimentally determined phase compositions very well, the incorporation of minor CaS leads to a modelled, although not experimentally found decrease of FeS solubility into the solid solution. The resulting bulge in the modelled solidus at the temperatures between 1100 and $1300\text{ }^{\circ}\text{C}$ towards MgS is likely the consequence of FeS showing a very low solubility in CaS ss_{cub} (cp. Figure 4) while the modelled effect of CaS on the behaviour of MgS ss_{cub} is too high. The likely reason for this can be found in the concept of our model, set up to use the lowest possible number of interaction parameters that reproduce the experimental data. More interaction parameters could have led to a smoother liquidus surface, but would have required a much more complicated model at the expense of easy applicability.

We in fact tested an approach with third-order terms for all systems but decided to only keep higher order terms that significantly improved the reproduction of the experimental data.

Conclusions

The phase diagrams, specifically the liquid–solid phase relations, of both the FeS–MgS and FeS–CaS binary systems and the FeS–MgS–CaS ternary system have been experimentally re-examined and modelled.

Experimental resolution in the FeS–MgS system together with the uncertainty in the melting point of pure troilite

prevents an accurate distinction between a eutectic or peritectic system, but is modelled as eutectic (at 2.5 mol% MgS at $1180\text{ }^{\circ}\text{C}$). The change in liquidus composition with temperature along the binary loop was found to be much more limited (i.e., a lower range of MgS contents) compared to previous experimental investigations. The difference of these experimental data compared to the only other available study are likely related to troilite vs. pyrrhotite (i.e., a slight S excess in the FeS phase) examined in preceding experiments.

The FeS–CaS system is a eutectic system with its invariant point at $7 \pm 1\text{ mol\% CaS}$ at $1063\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$. The difference of this experimental study to previous work, is the closed-system experimental approach employed in this work. Previous studies performed experiments that experienced constant sulfur loss and interaction of sulfide phases with the atmospheric O_2 . This study shows that, in particular, the compositions of CaS-rich phases are not readily determined by microbeam techniques (e.g., scanning electron microscopy) that compromises phase relations deduced from analytical, rather than textural, information.

The solvus in the MgS–CaS $_{\text{s.s.}}$ binary system has been re-evaluated. Compared to previous models, this solvus is predicted to close about $100\text{ }^{\circ}\text{C}$ higher, at a consolute point modelled to exist at $1210\text{ }^{\circ}\text{C}$. The closure of the solvus has been observed for the first time by experimental evidence. The liquidus of this system has been modelled from ternary experimental data.

The FeS–MgS–CaS ternary has also been experimentally studied in the temperature range between 1050 and $1360\text{ }^{\circ}\text{C}$. Our data are the first from an experimental investigation of the ternary system at these elevated temperatures to our knowledge. The most important feature is a 3-phase region that is present until $\sim 1250\text{ }^{\circ}\text{C}$. The three coexisting phases are two solid solutions, either high in MgS or CaS coexisting with a FeS phase, which is either pure and solid (below the eutectic temperature of the FeS–CaS binary) or liquid, containing both CaS and MgS in low amounts. Further, there is no evidence of liquid immiscibility in this system.

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Author contributions Stefan Pitsch conducted the experimental work, performed the data analysis, and wrote the manuscript. James Connolly provided the code for the thermodynamic evaluation and contributed to the analysis of the thermodynamic data. Max W. Schmidt, Paolo A. Sossi, and Christian Liebske provided supervision throughout the research, offered continued guidance on the interpretation of the laboratory results, and critically reviewed the manuscript.

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Data availability Data is provided within the manuscript or supplementary information files.

Declarations

Conflict of interest The authors declare no competing interests.

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References

- Andreev O, Solov'eva A, Burkhanova T (2006) MgS-FeS phase diagram. *Russ J Inorg Chem* 51(11):1826–1828
- Anzures BA et al (2020) Effect of sulfur speciation on chemical and physical properties of very reduced mercurian melts. *Geochim Cosmochim Acta* 286:1–18
- Bale CW et al (2009) FactSage thermochemical software and databases—recent developments. *Calphad* 33(2):295–311
- Barraud O, Doressoundiram A, Besse S (2021) Spectral curvature of hollows on Mercury as an indicator of their composition? *Copernicus Meetings*
- Carpenter RH, Desborough GA (1964) Range in solid solution and structure of naturally occurring troilite and pyrrhotite. *Am Mineral* 49(9–10):1350–1365
- Davies P, Navrotsky A (1983) Quantitative correlations of deviations from ideality in binary and pseudobinary solid solutions. *J Solid State Chem* 46(1):1–22
- Dilner D (2016) Thermodynamic description of the Fe-Mn-Ca-Mg-S system. *Calphad* 53:55–61
- Dilner D, Mao H, Selleby M (2015) Thermodynamic assessment of the Mn-S and Fe-Mn-S systems. *Calphad* 48:95–105
- Dilner D, Kjellqvist L, Selleby M (2016) Thermodynamic assessment of the Fe-Ca-S, Fe-Mg-O and Fe-Mg-S systems. *J Phase Equilib Diffus* 37(3):277–292
- Evans LG et al (2012) Major-element abundances on the surface of mercury: results from the MESSENGER gamma-ray spectrometer. *J Geophys Res* 117(E12)
- Fleet ME (2006) Phase equilibria at high temperatures. *Rev Mineral Geochem* 61(1):365–419
- Haberle C, Garvie L, Domanik K, Christensen P (2013) Metamorphic formation of extraterrestrial portlandite in the Sutter's Mill Meteorite (SM3). P31B-1809
- Hansen M, Anderko K, Salzberg H (1958) Constitution of binary alloys. *J Electrochem Soc* 105(12):260C
- Heumann T (1942) Die Löslichkeit von Eisensulfid in Kalziumsulfid bei der eutektischen Temperatur. *Archiv Für Das Eisenhüttenwesen* 15(12):557–558
- Jantzen T, Hack K, Yazhenskikh E, Müller M (2017a) Evaluation of thermodynamic data and phase equilibria in the system Ca-Cr-Cu-Fe-Mg-Mn-S Part II: ternary and quasi-ternary subsystems. *Calphad* 56:286–302
- Jantzen T, Hack K, Yazhenskikh E, Müller M (2017b) Evaluation of thermodynamic data and phase equilibria in the system Ca-Cr-Cu-Fe-Mg-Mn-S part I: binary and quasi-binary subsystems. *Calphad* 56:270–285
- Jensen E (1942) The field of stability of pyrrhotite. *EOS Trans Am Geophys Union* 23(2):347–347
- Juza R, Bünzen K (1958) Untersuchungen über das System Calciumcarbid/Calciumsulfid. *Z Phys Chem* 17(1–2):82–99
- Keil K (1968) Mineralogical and chemical relationships among enstatite chondrites. *J Geophys Res* 73(22):6945–6976
- Khan D, Liebske C, Connolly JA (2021) An algorithm for thermodynamic parameter optimization: application to the Martian mantle. *Geochim Geophys Geosyst* 22(5):e2020GC009399
- Kurat G, Zinner E, Brandstätter F, Ivanov A (2004) Enstatite aggregates with niningerite, heideite, and oldhamite from the Kaidun carbonaceous chondrite: relatives of aubrites and EH chondrites? *Meteorit Planet Sci* 39(1):53–60
- Larimer JW (1968) An experimental investigation of oldhamite, CaS; and the petrologic significance of oldhamite in meteorites. *Geochim Cosmochim Acta* 32(9):965–982
- Lawrence DJ et al (2013) Evidence for water ice near Mercury's north pole from MESSENGER Neutron Spectrometer measurements. *Science* 339(6117):292–296
- Lodders K (1996) An experimental and theoretical study of rare-earth-element partitioning between sulfides (FeS, CaS) and silicate and applications to enstatite achondrites. *Meteorit Planet Sci* 31(6):749–766
- Lunning N et al (2020) Insights into the formation of silica-rich achondrites from impact melts in Rumuruti-type chondrites. *Meteorit Planet Sci* 55(1):130–148
- Mann G, Van Vlack L (1976) FeS-MnS phase relationships in the presence of excess iron. *Metall Trans B* 7(3):469–475
- Moreau JG et al (2022) Bulk synthesis of stoichiometric/meteoritic troilite (FeS) by high-temperature pyrite decomposition and pyrrhotite melting. *Meteorit Planet Sci* 57(3):588–602
- Nittler LR et al (2011) The major-element composition of Mercury's surface from MESSENGER X-ray spectrometry. *Science* 333(6051):1847–1850
- Oshtakh M et al (2016) Iron sulfide (troilite) inclusion extracted from Sikhote-Alin iron meteorite: composition, structure and magnetic properties. *Mater Chem Phys* 174:100–111
- Peplowski PN et al (2012) Variations in the abundances of potassium and thorium on the surface of Mercury: results from the MESSENGER gamma-ray spectrometer. *J Geophys Res* 117(E12)
- Primak W, Kaufman H, Ward R (1948) X-ray diffraction studies of systems involved in the preparation of alkaline earth sulfide and selenide phosphors I. *J Am Chem Soc* 70(6):2043–2046
- Riner M, Lucey P, McCubbin F, Taylor G (2011) Constraints on Mercury's surface composition from MESSENGER neutron spectrometer data. *Earth Planet Sci Lett* 308(1–2):107–114
- Rochette P, Lorand J-P, Fillion G, Sautter V (2001) Pyrrhotite and the remanent magnetization of SNC meteorites: a changing perspective on Martian magnetism. *Earth Planet Sci Lett* 190(1–2):1–12
- Roine A (2002) HSC Chemistry, version 5.1. Outokumpu Research Oy, Pori, Finland
- Sack RO, Ebel DS (2006) Thermochemistry of sulfide mineral solutions. *Rev Mineral Geochem* 61(1):265–364
- Senuma T (2002) Present status of and future prospects for precipitation research in the steel industry. *ISIJ Int* 42(1):1–12
- Sharma RC, Chang Y (1979) Thermodynamics and phase relationships of transition metal-sulfur systems: Part III. Thermodynamic properties of the Fe-S liquid phase and the calculation of the Fe-S phase diagram. *Metall Trans B* 10:103–108
- Skinner BJ, Luce FD (1971) Solid solutions of the type (Ca, Mg, Mn, Fe) S and their use as geothermometers for the enstatite chondrites. *Am Mineral* 56(7–8):1269–1296
- Starr RD et al (2012) MESSENGER detection of electron-induced X-ray fluorescence from Mercury's surface. *J Geophys Res* 117(E12)
- Taylor L (1970) The system Ag-Fe-S: Phase relations between 1200 and 700 °C. *Metall Trans* 1:2523–2529

- Thomas JE, Skinner WM, Smart RS (2003) A comparison of the dissolution behavior of troilite with other iron (II) sulfides; implications of structure. *Geochim Cosmochim Acta* 67(5):831–843
- Vogel R, Heumann T (1941) Das System Eisen-Eisensulfid-Kalzium-sulfid. *Archiv Für Das Eisenhüttenwesen* 15(4):195–199
- Walder P, Pelton AD (2005) Thermodynamic modeling of the Fe-S system. *J Phase Equilib Diffus* 26:23–38
- Weider SZ et al (2015) Evidence for geochemical terranes on Mercury: global mapping of major elements with MESSENGER's X-ray spectrometer. *Earth Planet Sci Lett* 416:109–120
- Weider SZ et al (2012) Chemical heterogeneity on Mercury's surface revealed by the MESSENGER X-ray spectrometer. *J Geophys Res* 117(E12)
- Whitby JA, Gilmour J, Turner G, Prinz M, Ash R (2002) Iodine-Xenon dating of chondrules from the Qingzhen and Kota Kota enstatite chondrites. *Geochim Cosmochim Acta* 66(2):347–359
- Yan J, Li T, Shang Z, Guo H (2019) Three-dimensional characterization of MnS inclusions in steel during rolling process. *Mater Charact* 158:109944
- Zekker I, Tenno T, Selberg A, Uiga K (2011) Dissolution modeling and experimental measurement of CaS-H₂O binary system. *Chin J Chem* 29(11):2327–2336
- Zlomanov VP, Novoselova AV (1987) P–T–x Diagrams for Metal–Chalcogen Systems Nauka, Moscow
- Zvimba J, Mulopo J, De Beer M, Bologo L, Mashego M (2011) The dissolution characteristics of calcium sulfide and utilization as a precipitation agent in acidic wastewater effluent treatment. *Water Sci Technol* 63(12):2860–2866

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