

Article

Melting Processes of Pelitic Rocks in Combustion Metamorphic Complexes of Mongolia: Mineral Chemistry, Raman Spectroscopy, Formation Conditions of Mullite, Silicate Spinel, Silica Polymorphs, and Cordierite-Group Minerals

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Citation: Peretyazhko, I.S.; Savina, E.A. Melting Processes of Pelitic Rocks in Combustion Metamorphic Complexes of Mongolia: Mineral Chemistry, Raman Spectroscopy, Formation Conditions of Mullite, Silicate Spinel, Silica Polymorphs, and Cordierite-Group Minerals. *Geosciences* **2023**, *13*, 377. <https://doi.org/10.3390/geosciences13120377>

Academic Editors: Jesus Martinez-Frias and Jaime Cuevas Rodríguez

Received: 10 November 2023

Revised: 8 December 2023

Accepted: 8 December 2023

Published: 11 December 2023



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Abstract: Melted rocks (clinkers and paralavas) of the Mongolian combustion metamorphic (CM) complexes were formed during modern and ancient (since the Quaternary) wild-fires of brown coal layers in the sedimentary strata of the Early Cretaceous Dzunbain Formation. According to XRD, Raman spectroscopy, and SEM-EDS data, cordierite, sekaninaite, indialite, ferroindialite, silica polymorphs, mullite, Fe-mullite, anhydrous Al-Fe-Mg silicate spinel (presumably new mineral), and other phases were identified. It has been established that isomorphic impurity of potassium in the cordierite-group minerals does not correlate with their crystal structure (hexagonal or orthorhombic). Indialite and ferroindialite retained their hexagonal structure in some fragments of the CM rocks, possibly due to the very fast cooling of local zones of sedimentary strata and the quenching of high-temperature K-rich peraluminous melt. Clinkers, tridymite–sekaninaite, and cristobalite–fayalite ferroan paralavas were produced by partial melting of Fe-enriched pelitic rocks (mudstone, siltstone, and silty sandstone) in a wide temperature range. The formation of mullite, Fe-mullite, and Al-Fe-Mg silicate spinel in clinkers developed from dehydration–dehydroxylation and incongruent partial melting of Fe-enriched pelitic matter (Al-Mg-Fe-rich phyllosilicates, ‘meta-kaolinite’, and ‘meta-illite’). Large-scale crystallization of these minerals in the K-rich peraluminous melts occurred, presumably, in the range of $T > 850\text{--}900\text{ }^{\circ}\text{C}$. The subsurface combustion of coal layers heated the overburden pelitic rocks from sedimentary strata to $T > 1050\text{ }^{\circ}\text{C}$ (judging by the formation of cordierite-group minerals) or locally till the melting point of detrital quartz grains at $T > 1300\text{ }^{\circ}\text{C}$ and, possibly, till the stability field of stable β -cristobalite at $T > 1470\text{ }^{\circ}\text{C}$. Ferroan paralavas were formed during the rapid crystallization of Fe-rich silicate melts under various redox conditions. From the analysis of the liquidus surface in the $\text{Al}_2\text{O}_3\text{--FeO--Fe}_2\text{O}_3\text{--SiO}_2$ major-oxide system, it follows that the least high-temperature ($<1250\text{ }^{\circ}\text{C}$) and the most oxidizing conditions occurred during the crystallization of mineral assemblages in the most-enriched iron silicate melts parental for cristobalite–fayalite paralava.

Keywords: combustion metamorphic complex; cristobalite clinker; tridymite–sekaninaite and cristobalite–fayalite ferroan paralavas; melting processes; Raman spectroscopy; cordierite-group minerals; silica polymorphs; mullite; Al-Fe-Mg silicate spinel; Mongolia

1. Introduction

In Central and Eastern Mongolia, we discovered and are still studying in detail the processes and formation conditions of two combustion metamorphic (CM) complexes (Nyalga and Khamaryn–Khural–Khiid), located at distances about 300 km from each other (Figure 1a). The complexes contain melted rocks to varying degrees (clinkers and paralavas), formed during modern and ancient (since the Quaternary) wild-fires of brown coal layers in the sedimentary strata of the Early Cretaceous Dzunbain Formation [1–6].

Clinkers and paralavas are formed through the melting of diverse types of dehydrated and partially decarbonated sedimentary protolith in response to caustobiolith (coals, bitumens, and natural gas) fires [7,8]. Currently, there is no generally accepted classification of CM rocks. Term clinker refers to the partially melted pelites and metapelites containing acid glass [7–10]. Paralavas are the full melting products of carbonate–silicate sedimentary rocks, and show wide variations of rock-forming elements (Si, Al, Fe, Ca, and Mg) [8–11]. Paralavas frequently have no compositional analogs among igneous and volcanic rocks.

The Nyalga CM complex belongs to the Choir–Nyalga coal-bearing basin of Central Mongolia [12]. In the area of the CM complex, three outliers up to 40 m high were discovered (Crown, Camel, and Baby) composed of melted rocks, which were preserved after erosion of the sedimentary strata [1,2] (Figure 1b). The CM rocks are thermally modified mudstones–siltstones and the products of their partial melting—glassy clinker (Figure 1c,d). On the outcrops and eroded surface near them, with an area of ~20 km², there are debris and single blocks of melilite–nepheline paralava (Figure 1e). Clinkers and paralava contain xenoliths ranging in size from fractions of a mm to several cm of baked sedimentary rocks. Near ~5 km to the southeast of the outliers there is the Tugrug coal quarry, on the walls of which sedimentary strata are exposed, locally with CM rocks (Figure 1c). Near the quarry, blocks of massive crystallized plagioclase–pyroxene ± indialite paralava without melilite and nepheline were discovered.

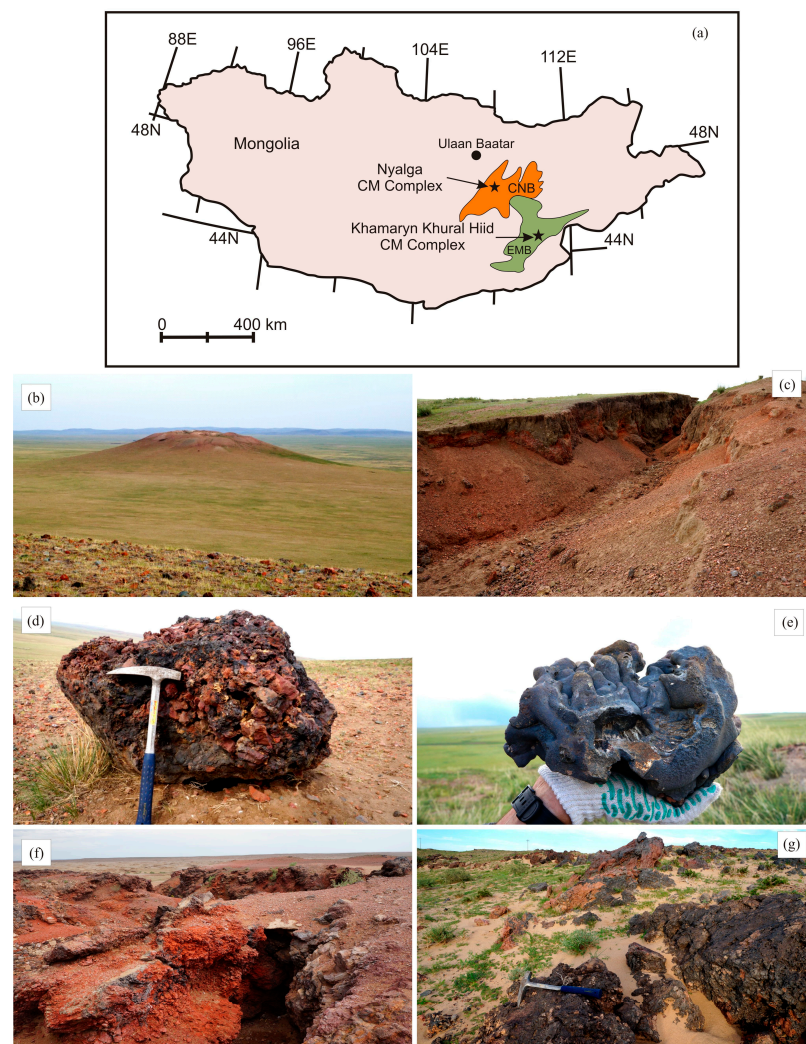


Figure 1. Location map (a) of the Choir–Nyalga Basin (CNB) and the Eastern Mongolian Basin (EMB) modified after [12], stars coordinates of the CM complexes: Nyalga 46°53′07″ N, 108°02′55″ E, and

Khamaryn–Khural–Khiid 44°36′56″ N, 110°16′42″ E. (b–e) Nyalga: remnant of eroded layered sediments strata, Crown outlier (b), baked pelitic rocks exposed by a ravine near the Tugrug coal quarry (c), block of sintered fragments of baked siltstone and clinker (d), melilite–nepheline paralava having signatures of melt flow on the sample surface (e). (f,g) Khamaryn–Khural–Khiid: collapse failures of CM rocks (e), bedrock outcrops of cristobalite clinker, and baked or partly melted silty sandstone (g).

The Khamaryn–Khural–Khiid CM complex is located in Eastern Mongolia (Figure 1a). The CM rocks of the complex form a modern landscape with extended ridges, numerous ravines and small caves formed after the collapse of sedimentary strata over burnt coal layers (Figure 1f,g). The last coal fire was observed here in 1932–1947 [13]. In the central part of the complex, the thickness of baked pelitic rocks and melted CM rocks containing sintered fragments of thermally modified mudstone, siltstone, silty sandstone, glassy clinker, and melilite–nepheline paralava reaches 30–50 m. The results of the mineralogical and geochemical study of pelitic rocks, marly limestone remnants, clinkers, and melilite–nepheline paralava are provided in [3–6].

We report a synthesis of data on mineral assemblages of clinkers and ferroan paralavas from the above-described CM complexes. Mineral chemistry and confocal Raman spectroscopy data of the rock-forming minerals are discussed: mullite, Fe–mullite, anhydrous Al–Fe–Mg silicate (presumably new spinel-group mineral), silica polymorphs (quartz, tridymite, and cristobalite), cordierite, sekaninaite, indialite, and ferroindialite. Based on the analysis of the nonequilibrium conditions of mullite crystallization in metamorphic and CM rocks, as well as the liquidus surface in the Al_2O_3 –FeO–Fe $_2\text{O}_3$ –SiO $_2$ major-oxide system, the processes and conditions of partial melting of Fe-rich pelitic rocks caused by underground coal fires are discussed. Temperatures and redox conditions for the crystallization of rock-forming mineral assemblages in cristobalite clinker, tridymite–sekaninaite and cristobalite–fayalite ferroan paralavas are analyzed.

2. Materials and Methods

The collected samples were analyzed at the Center for Isotope-Geochemical Studies of the Vinogradov Institute of Geochemistry, Siberian Branch of the Russian Academy of Sciences (IGC, Irkutsk). Minerals and phases in CM rocks were investigated by scanning electron microscopy coupled with energy-dispersive spectrometry (SEM EDS) on a *Tescan Mira 3* LMU microscope with an ULTIM MAX 40 microanalysis system (Oxford Instruments). The analyses were performed in a scanning mode on carbon-coated polished cut surfaces of samples, at 1 to and over $>10\ \mu\text{m}^2$ rectangular spots, 20 kV accelerating voltage, 1 nA beam current, and 30 s data-collection time (excluding dead time). The quality was checked against analyses of reference samples, including quartz, albite, orthoclase, wollastonite, MgO, Al_2O_3 , CaF_2 , metals, and synthetic compounds from sets 6316 and 7682 of the reference standards by Microanalysis Consultants Limited (Oxford Instruments Ltd., UK). All the calculations and matrix corrections were conducted automatically by AZtec software (Oxford Instruments Nanoanalysis, UK). The detection limits of major elements were 0.2–0.3 wt%. Average random errors were different, depending on the contents of major elements: $\pm 0.9\ \text{rel}\%$ at $>10\ \text{wt}\%$, $\pm 3.0\ \text{rel}\%$ at 1–10 wt%, and $\pm 13\ \text{rel}\%$ at 0.3–1 wt% [14]. The crystal chemical formulas were calculated using the *Crystal* software, ver. 3.0 [15].

Thin sections were studied by optical and ore microscopy by means of an Olympus BX-41. Powdered samples were analyzed by X-ray powder diffraction (XRD) on a Bruker *D8 ADVANCE* diffractometer equipped with a *VANTEC-1* PSD detector at 2θ from 3 to 70° , with $\text{CuK}\alpha$ radiation. The operating conditions were: 40 kV accelerating voltage, 40 mA beam current, 1 s counting time, and stepsize $0.02^\circ\ 2\theta$. The crystalline phases were identified using the *EVA* software ver. 3.1 (Bruker) with reference to the PDF-2 (ICDD) database.

Using XRD, it is impossible to diagnose many accessory minerals, due to their small quantity and the overlap of peaks of some main rock-forming phases in the powder

diffraction patterns. Therefore, in addition to XRD, mineral diagnostics were carried out (refined) using SEM-EDS and confocal Raman spectroscopy.

The Raman spectra were performed on a WITec confocal *Alpha 300R* (WITec GmbH) spectrometer with 532 nm Nd:YAG laser excitation (1–22 mW), at the Analytical Center Geodynamics and Geochronology in the Institute of the Earth's Crust (Irkutsk). The ~1–2 μm laser beam was focused using a Zeiss lens 100x. The spectra were collected in the 100 to 4000 cm^{-1} range, in 3 to 50 acquisition cycles of 10 to 50 s, depending on peak intensity, at an optical resolution of 1800 gr/mm and 600 gr/mm. Spectra calibration was according to the 520.7 cm^{-1} band for crystalline Si, and mineral phases were identified with reference to the RRUFF database (<http://rruff.info/>) [16] (accessed on 9 November 2023).

3. Results

3.1. Thermally Modified Pelitic Rocks and Clinkers

Pelitic rocks (mudstones, siltstones, and silty sandstones), burned during the combustion of underlying layers of brown coal in sedimentary strata, as well as their partly or completely melted varieties (clinkers), are most characteristic for thermally modified sedimentary strata in the CM complexes of Mongolia. On the TAS diagram (SiO_2 vs. $\text{Na}_2\text{O} + \text{K}_2\text{O}$) of volcanic rocks, mudstones, siltstones, and glassy clinkers are in the dacite field and sandstones—silty sandstones are in the rhyolite field [2–4].

Clinkers often contain xenoliths of the parent pelitic rock, surrounded by glassy zones. Minerals of the cordierite-group, quartz and mullite, were diagnosed in clinker samples using XRD. In addition, according to SEM-EDS and Raman spectroscopy, the clinkers contain K-rich peraluminous glass, feldspars, Fe and Ti oxides, grains of detrital quartz, zircon, monazite, and other accessory minerals.

The most diverse mineral-phase assemblages are characteristic of cristobalite clinker in the Khamaryn–Khural–Khiid CM complex. The clinker matrix is highly heterogeneous and consists of vitreous and partly crystallized zones with numerous elongate cristobalite grains and anhedral fine particles (microliths) of cordierite-group minerals, often with cristobalite inclusions (Figure 2a,b); glass zones free from inclusions are $\leq 20\text{--}30\ \mu\text{m}$ in size. The partly crystallized matrix zones enclose numerous acicular $<1\text{--}3\ \mu\text{m}$ microliths of mullite and grains of anhydrous Si–Al–Fe–Mg silicates, large grains of Ti-magnetite, ulvöspinel, Al-spinel, ferrosilite, and rare fayalite with interstitial cristobalite or high-silica K-rich peraluminous glass. Often there are grains of detrital quartz surrounded by a cristobalite rim ($5\text{--}20\ \mu\text{m}$) and elongated cristobalite crystals. Clinker in the sample MN-1403 also has vitreous zones with dendritic or hopper crystals of cordierite-group minerals, often hexagonal, and elongate anorthite–bytownite microliths with cristobalite in-between (intergrowths in Figure 2c–f).

XRD analysis of clinker samples MN-1402, MN-1405, and MN-1403 revealed orthorhombic and hexagonal grains of cordierite-group minerals with zero distortion index: $\Delta = 2\theta_{131} - (2\theta_{511} + 2\theta_{421})/2$, according to [17,18]. Powder-diffraction patterns show symmetrical or asymmetrical $\sim 3.06\ \text{\AA}$ peaks with a half-width of $0.22\text{--}0.31^\circ 2\theta$, which is typical of hexagonal indialite or ferroindialite. Sample MN-1408 shows only orthorhombic cordierite–sekaninaite (triplet in the $29\text{--}30^\circ 2\theta$ region, $\Delta = 0.2 - 0.3$).

3.2. Ferroan Paralavas

Massive crystallized ferroan paralavas with signatures of melt flow on the sample surface containing 19–42 wt% Fe_2O_3 tot are rare in the Khamaryn–Khural–Khiid CM complex. These paralavas have no analogs in bulk and mineral-phase compositions among igneous and volcanic rocks.

3.2.1. Tridymite–Sekaninaite Paralava

According to SEM-EDS, XRD, and Raman spectroscopy, the two samples of tridymite–sekaninaite paralava (MN-1363 and MN-1368) containing 19–23 wt% Fe_2O_3 tot are compositionally similar and mainly consist of tridymite, sekaninaite, and lesser amounts of

fayalite, Ti-magnetite, ferrosilite, and high-silica K-rich peraluminous glass (Figure 3a–d). Fayalite grains produce spinifex-like textures with ~1 mm long randomly oriented acicular clusters. Accessories include anorthite–bytownite, hyalophane–celsian, Al-spinel, fluorapatite, barite, and calcite. The paralava samples also contain sporadic partly melted and dissolved grains of detrital quartz rimmed with tridymite at the contact with the matrix and containing cristobalite veinlets (Figure 4). Some quartz grains in the tridymite–sekaninaite matrix of sample MN-1368 have cristobalite rims and acicular cristobalite microliths up to 5–7 μm (Figure 3c).

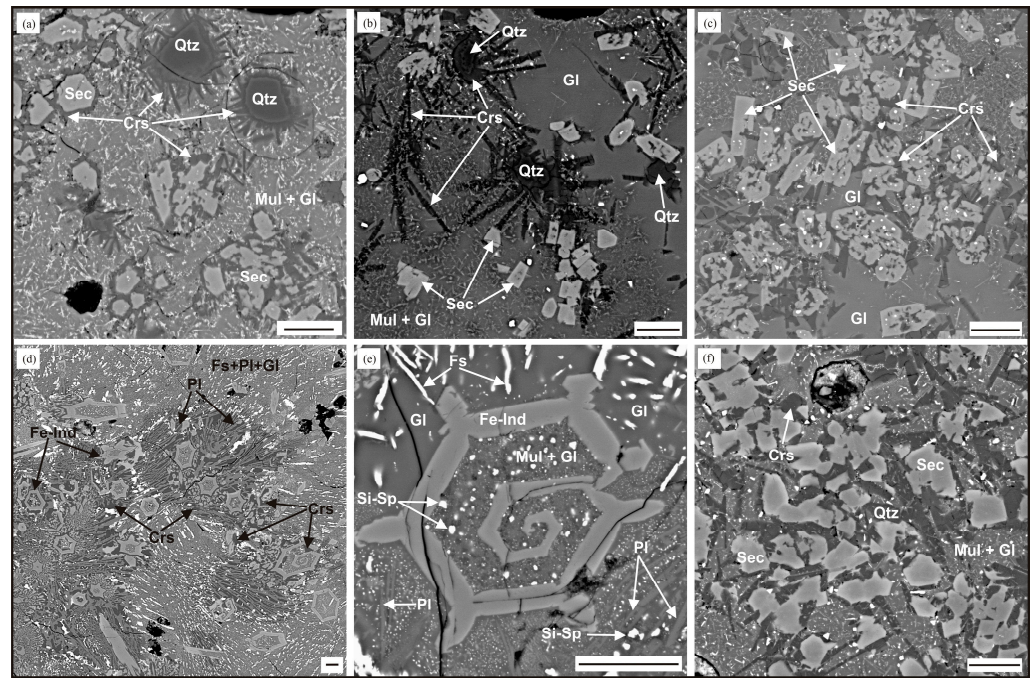


Figure 2. Matrix fragments of cristobalite clinker, BSE images. (a) Poorly defined microliths of sekaninaite–cordierite in K-rich peraluminous glass containing partly melted quartz grains, acicular cristobalite, mullite, Fe-mullite, Al-Fe silicate spinel, and Fe and Ti oxides, sample MN-1365. (b,c) Microliths of sekaninaite in glass zone free from inclusions and partly crystallized zones with cristobalite, sekaninaite, and mullite, sample MN-1408. (d–f) Sample MN-1403: dendritic ferroindialite–indialite intergrowths with cristobalite and plagioclase (d), dendritic hopper ferroindialite crystal in a vitreous zone enclosing mullite, Fe-mullite, Al-Fe silicate spinel, and acicular ferrosilite (e), sekaninaite–cordierite microliths (f). Scale bar is 20 μm in all panels. Sec = sekaninaite, Fe-Ind = ferroindialite, Crs = cristobalite, Gl = glass, Mul = mullite and Fe-mullite, Qtz = detrital quartz, Pl = plagioclase, Fs = ferrosilite, Si-Sp = Al-Fe silicate spinel.

3.2.2. Cristobalite–Fayalite Paralava

The matrix of the most ferroan paralava containing up to 42 wt% Fe_2O_3 tot is characterized by large needle-shaped dendrites measuring 1–3 mm in elongation, composed of isometric grains (20–40 μm) of fayalite and Al-magnetite, which form the spinifex-like structure (Figure 3e,f). The interstices are mainly filled with rock-forming cristobalite or locally with small dendritic plagioclase and K-Na feldspar in small zones of high-silica K-rich peraluminous glass. Accessory phases include fluorapatite and Fe-Mn-Ca phosphate, presumably from the graftonite-group (Figure 3f), with ideal crystal chemical formula $(\text{Fe}^{2+}\text{MnCa})_3(\text{PO}_4)_2$ [19,20]. Vugs in the matrix are filled with supergene secondary phases: goethite, jarosite, calcite, and unidentified Si-Fe-P- H_2O -bearing phases. The ferroan paralava bears grains of detrital quartz and fused vitreous pelitic xenoliths consisting of intergrowths < 1 μm of cristobalite and sekaninaite $\pm$ plagioclase and Al-magnetite.

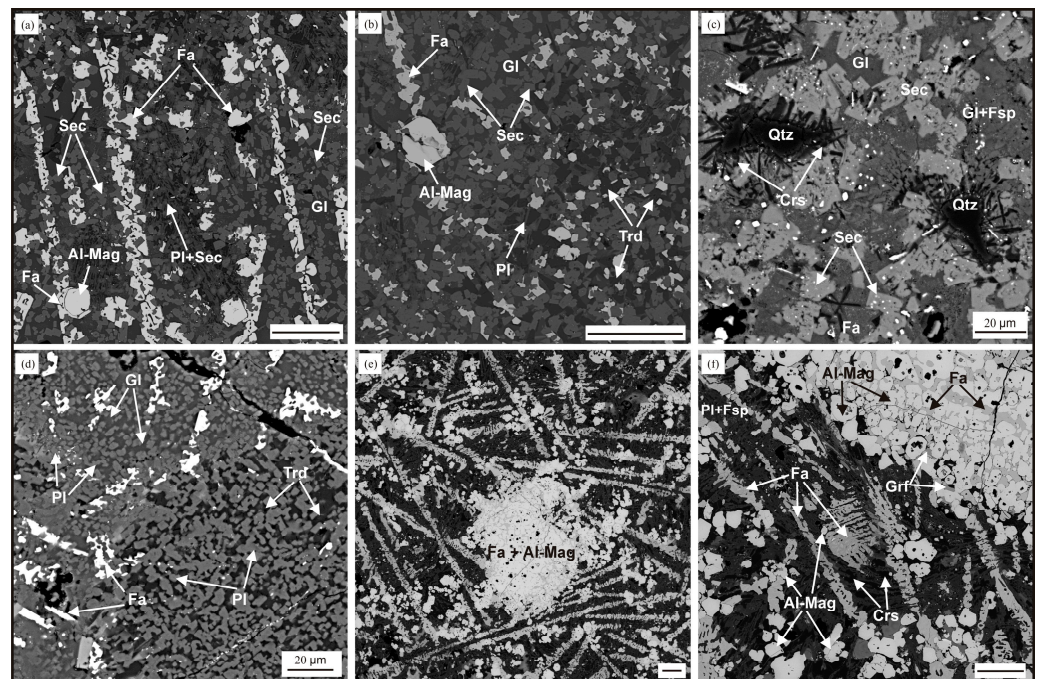


Figure 3. Matrix fragments of ferroan paralavas, BSE images. (a–d) Tridymite–sekaninaite paralava: spinifex-like texture (dendritic fayalite) in partly crystallized tridymite–sekaninaite matrix, sample MN-1363 (a); dendritic fayalite, Al-magnetite and anorthite–bytownite microlithes, sample MN-1363 (b); partly melted quartz grains containing acicular cristobalite microliths in tridymite–sekaninaite matrix, enclosing glass, mullite, Al-Fe silicate spinel, anorthite–bytownite, and Fe-Ti oxides, sample MN-1368 (c); matrix enclosing tridymite–sekaninaite and glass–sekaninaite zones, inclusions of anorthite–bytownite and fayalite, sample MN-1368 (d). (e,f) Cristobalite–fayalite paralava matrix, enclosing fayalite, Al-magnetite, cristobalite, anorthite–bytownite, K-Na feldspar, and rare grains of mineral presumably from the graftonite-group, sample MN-1370. Scale bar is 100 μm in all panels, if not indicated otherwise. Trd = tridymite, Fa = fayalite, Pl = plagioclase, Gl = glass, Al-Mag = Al-magnetite, Fsp = K-Na feldspar, Grf = graftonite-group mineral.

3.3. Rock-Forming Minerals of Clinkers and Ferroan Paralavas

3.3.1. Cordierite-Group Minerals: Raman Spectroscopy, and Compositional Variations

Confocal Raman spectroscopy can resolve cordierite-group minerals in local micrometer grains or inclusions [1,2]. The Raman spectra of indialite are known from experimental data to have fewer and smaller peaks than cordierite in the 100–1250 cm^{-1} region [21]. The Raman spectra of disordered hexagonal and ordered orthorhombic (pseudo-hexagonal) cordierite-group minerals were described earlier in clinkers and plagioclase–pyroxene–indialite paralava from the Nyalga CM complex: broad peaks with maximums around 567 cm^{-1} for indialite and ferroindialite and two peaks in the 557–578 cm^{-1} range for cordierite [1].

In the clinker sample MN-1129 from the Nyalga CM complex, we studied in detail the Raman spectra and determined the composition of cordierite-group minerals: hexagonal crystals located in K-rich peraluminous glass – phenocryst $40 \times 50 \mu\text{m}$ and microliths 10–15 μm in cross section (Figure 5). Phenocrysts and glass often contain small (<2–3 μm) inclusions and grains of mullite and anhydrous Al-Fe-Mg silicates of the spinel structural type (see description below). According to Raman spectra and SEM-EDS, the orthorhombic phase most-magnesian cordierite ($\text{Mg}\#, \text{Mg}/(\text{Mg} + \text{Fe}^{2+}) = 0.64\text{--}0.75$) crystallizes in the core zone of a large phenocryst, and the hexagonal phase of Fe-rich indialite ($\text{Mg}\# = 0.56\text{--}0.67$) crystallizes in the outer (rim) zone of phenocryst and in microliths (Figure 5d–g, Table S1). We note a constant admixture of potassium and an increase in its

content from 0.03–0.07 apfu (0.2–0.5 wt% K_2O) in cordierite to 0.05–0.14 apfu (0.3–1.1 wt% K_2O) in Fe-rich indialite.

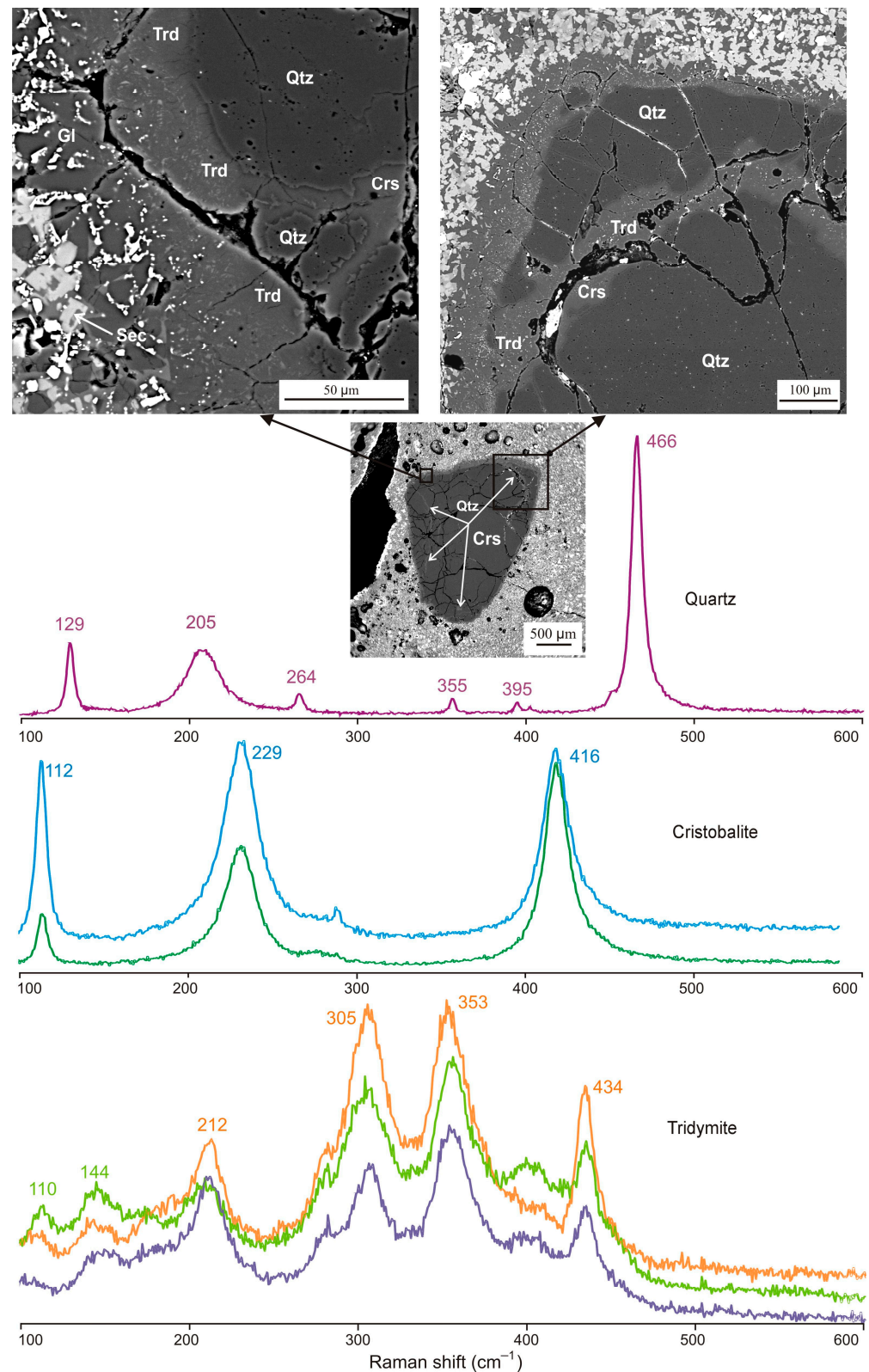


Figure 4. Partly melted and dissolved detrital quartz grain in the matrix of tridymite–sekaninaite paralava, sample MN-1363. The quartz grain contains numerous thin veinlets of cristobalite, and a tridymite rim. Typical Raman spectra of quartz, α -cristobalite, and α -tridymite are shown.

Raman spectra and compositions of cordierite-group minerals differ, especially in cristobalite clinker samples from the Khamaryn–Khural–Khiid CM complex, where dendritic and hexagonal hopper crystals of a phase intermediate between indialite and ferroindialite are often present in glassy clinker matrix, while other zones samples bear only cordierite–sekaninaite (Figures 6 and 7, Table S1). Cordierite with the highest Mg#, $\text{Mg}/(\text{Mg} + \text{Fe}^{2+} + \text{Mn}) = 0.62$, at an average of 0.53–0.55, is rock-forming in samples MN-1365 and MN-1405 (Figures 2a and 7). The former contains a few dendritic ferroindialite crystals ($\text{Mg}\# = 0.2\text{--}0.4$), while clinker sample MN-1408 bears approximately equal percentages of unzoned cordierite ($\text{Mg}\# = 0.5\text{--}0.6$) and sekaninaite ($\text{Mg}\# = 0.4\text{--}0.5$) phenocrysts (Figures 2b,c and 7). The Mg# range is the largest (0.3–0.6) in cordierite-group minerals from sample MN-1403, where both microliths and dendritic indialite and ferroindialite crystals coexist with cordierite and sekaninaite in high-silica K-rich peraluminous glass and in intergrowths with cristobalite (Figures 2d–f and 7).

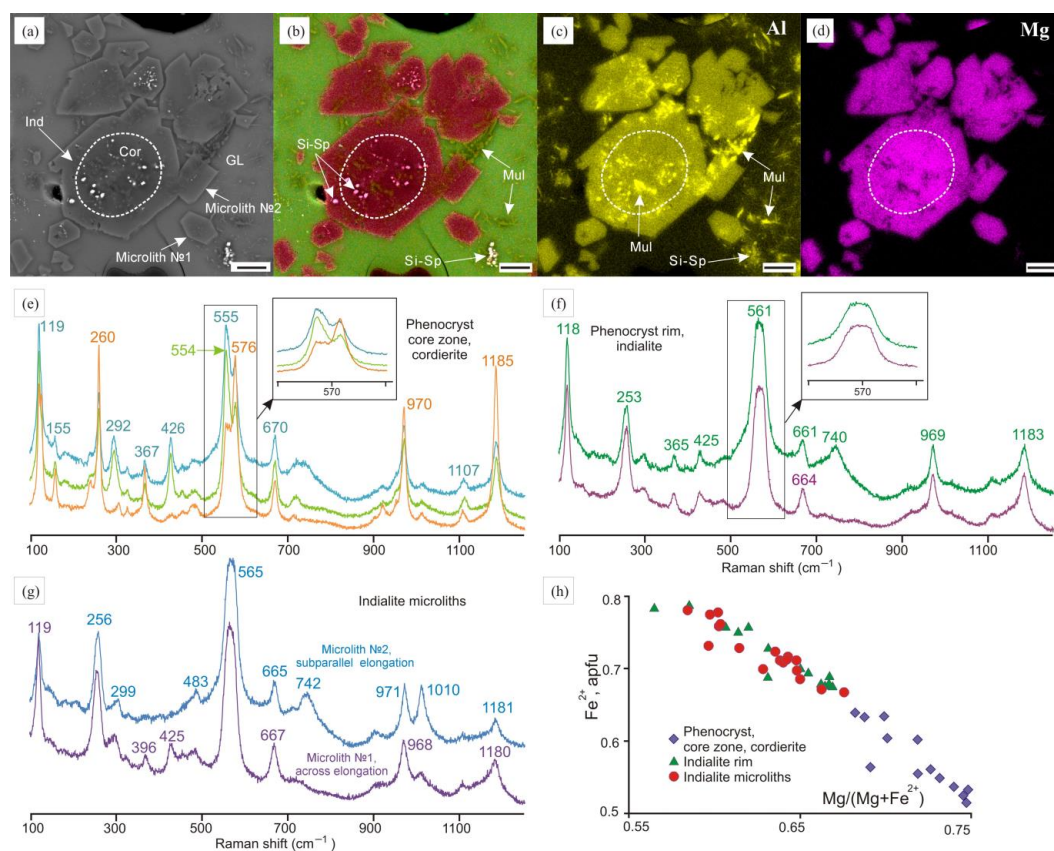


Figure 5. Zoned cordierite–indialite phenocryst and indialite microliths in K-rich peraluminous glass, clinker sample MN-1129. The phenocryst is composed of cordierite in the core zone (the outline is

shown by a dashed line), and indialite is found in the phenocryst rim and in microliths. Phenocryst and glass contain inclusions of mullite and Al–Fe–Mg silicate spinel. (a–d) SEM data, scale bar is 10 μm in all panels: BSE image (a), multilayer color map (b), Al K α (c), Mg K α (d). (e–g) Raman spectra of zoned cordierite–indialite phenocryst and indialite microliths in different sections. (h) Variations in the content of phenocrysts and microliths in the $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ vs. Fe^{2+} diagram (See Table S1 for mineral chemistry and formulas). Cor = cordierite, Ind = indialite, Mul = mullite, Si–Sp = Al–Fe–Mg silicate spinel (see Raman spectra, Figure 8b).

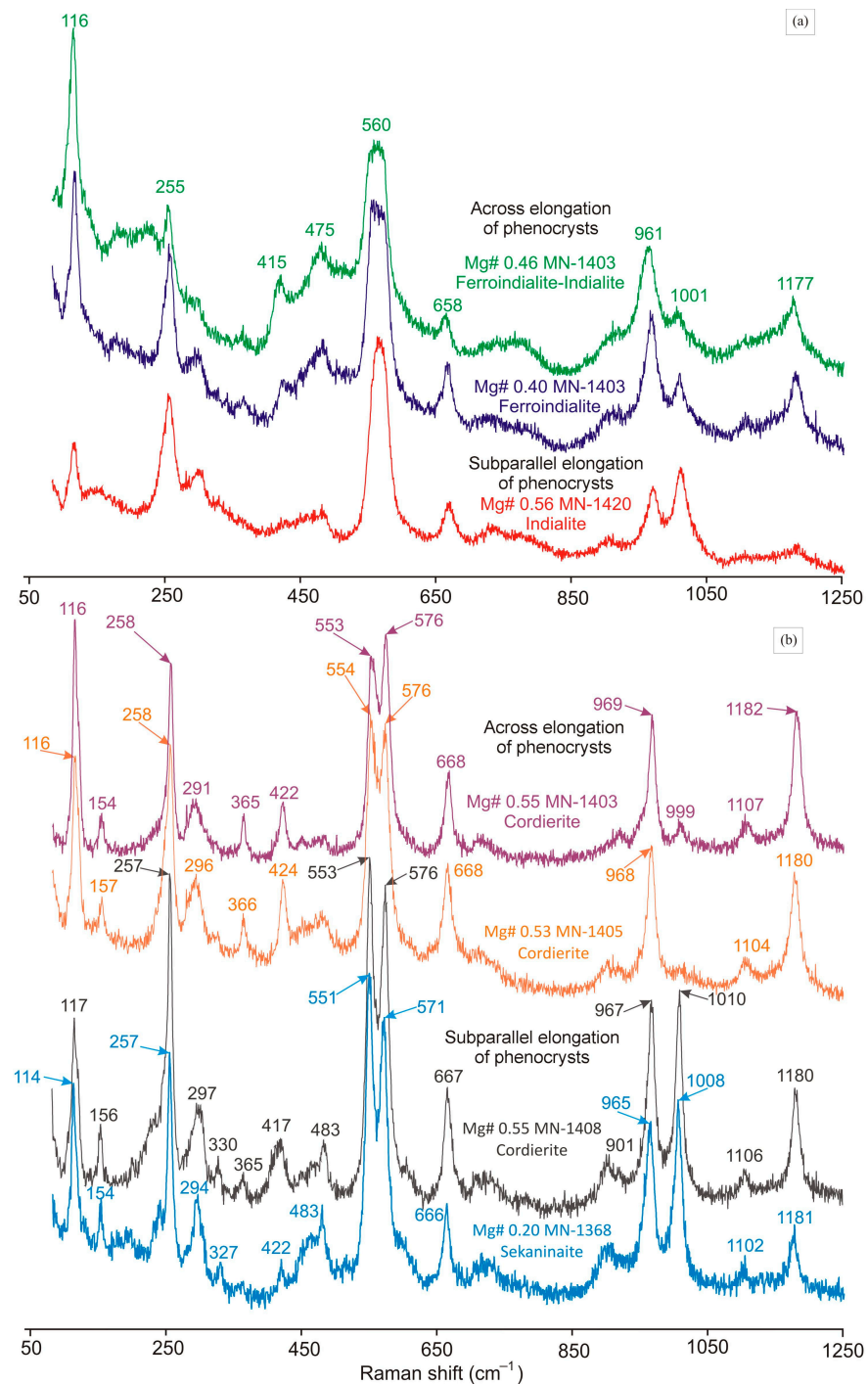


Figure 6. Raman spectra of cordierite-group minerals in cristobalite clinker (samples MN-1403, MN-1408, MN-1405) (a,b), tridymite–sekaninaite paralava (sample MN-1368) (b), and clinker xenoliths in melilite–nepheline paralava (sample MN-1420) (a). See Table S1 for mineral chemistry and formulas.

Rock-forming sekaninaite in tridymite–sekaninaite paralava samples MN-1363 and MN-1368 has the highest iron contents and a narrow Mg# range of 0.15 to 0.24. Raman spectra reveal indialite or cordierite and ferroindialite in cristobalite clinker xenoliths from melilite–nepheline paralava sample MN-1420, at an average Mg# of 0.55, or indialite–ferroindialite, at Mg# = 0.38 on average, in cristobalite–fayalite paralava sample MN-1370 (Figures 6 and 7a,c, Table S1).

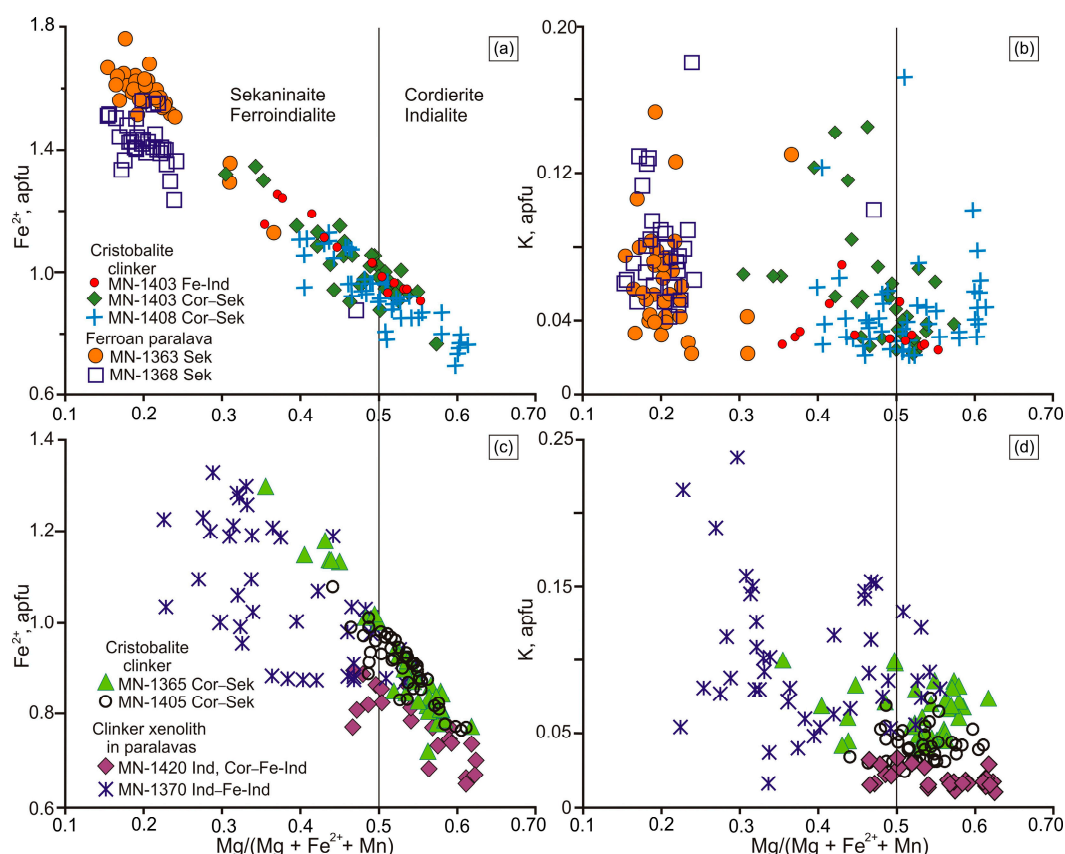


Figure 7. Cordierite-group minerals in the $\text{Mg}/(\text{Mg} + \text{Fe}^{2+} + \text{Mn})$ vs. Fe^{2+} (a,c) and vs. K (b,d) diagrams. See Table S1 for mineral chemistry and formulas. Cor = cordierite, Sek = sekaninaite, Ind = indialite, Fe-Ind = ferroindialite.

A characteristic feature of the composition of the cordierite-group minerals in Kamaryn–Khural–Khid CM rocks is the increased average K value (0.3–1.3 wt% K_2O , 0.04–0.17 apfu K) in the orthorhombic (cordierite–sekaninaite) relative to the hexagonal (indialite–ferroindialite) phases, containing an average of 0.2–0.5 wt% K_2O , 0.02–0.07 apfu K (Figure 7b,d). In addition, cordierite-group minerals have impurities: 0.2–0.5 wt% TiO_2 , sometimes up to 0.3 wt% CaO and up to 0.2 wt% Na_2O in the rim of phenocrysts. Cordierite–sekaninaite in clinker sample MN-1408 contains 0.2–0.3 wt% MnO, and the highest concentration of MnO is found in cordierite-group minerals in clinker xenoliths from cristobalite–fayalite paralava (Table S1, sample MN-1370, 0.5–1.3 wt% MnO) and tridymite–sekaninaite paralava (Table S1, sample MN-1368, 1–3 wt% MnO).

Cordierite-group minerals with different proportions of Mg and Fe are rather similar in their Raman spectra peak values but are strongly different in intensity, depending on structural features (orthorhombic or hexagonal [21]) and orientation of crystals of phenocrysts and microliths in random sections. In the Raman spectra (range 850–1250 cm^{-1}) of pseudohexagonal (for cordierite and sekaninanite) or hexagonal (for indialite and ferroindialite) sections across the crystals (phenocrysts and microliths) elongation, the most intense peaks are 961–969 cm^{-1} and 1177–1181 cm^{-1} , and in rectangular and square sections, subparallel to the crystals elongation, the peaks are 965–969 cm^{-1} and 1008–1110 cm^{-1} (Figures 5 and 6).

3.3.2. Mullite

The small sizes of needle-shaped crystals and grains of submicron and micron sizes (<1–2, rarely up to 3 μm) of mullite and other Al-Fe-Mg silicates do not allow determining their quantitative compositions. Estimated qualitatively, mullite $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$

($x = 0.2 - 0.9$) can be confused with sillimanite $\text{Al}_2(\text{SiO}_4)\text{O}$ or zunyite $\text{Al}_{13}\text{Si}_5\text{O}_{20}(\text{OH},\text{F})_{18}\text{Cl}$ which have similar SiO_2 and Al_2O_3 contents, and its peaks overlap with other phases at the sites of SEM-EDS analysis.

Mullite in clinkers was identified from more or less strong $\sim 300, 410, 450, 595, 670, 955, 1030$, and 1123 cm^{-1} bands in Raman spectra (Figure 8a), which showed no H_2O and OH^- bands between 3000 and 3600 cm^{-1} . The shape and position of prominent peaks ($\sim 300, 400, 600$, and 960 cm^{-1}) are similar to those in the spectra of natural mullite from Mull Island [22] and reference samples in the RRUFF database.

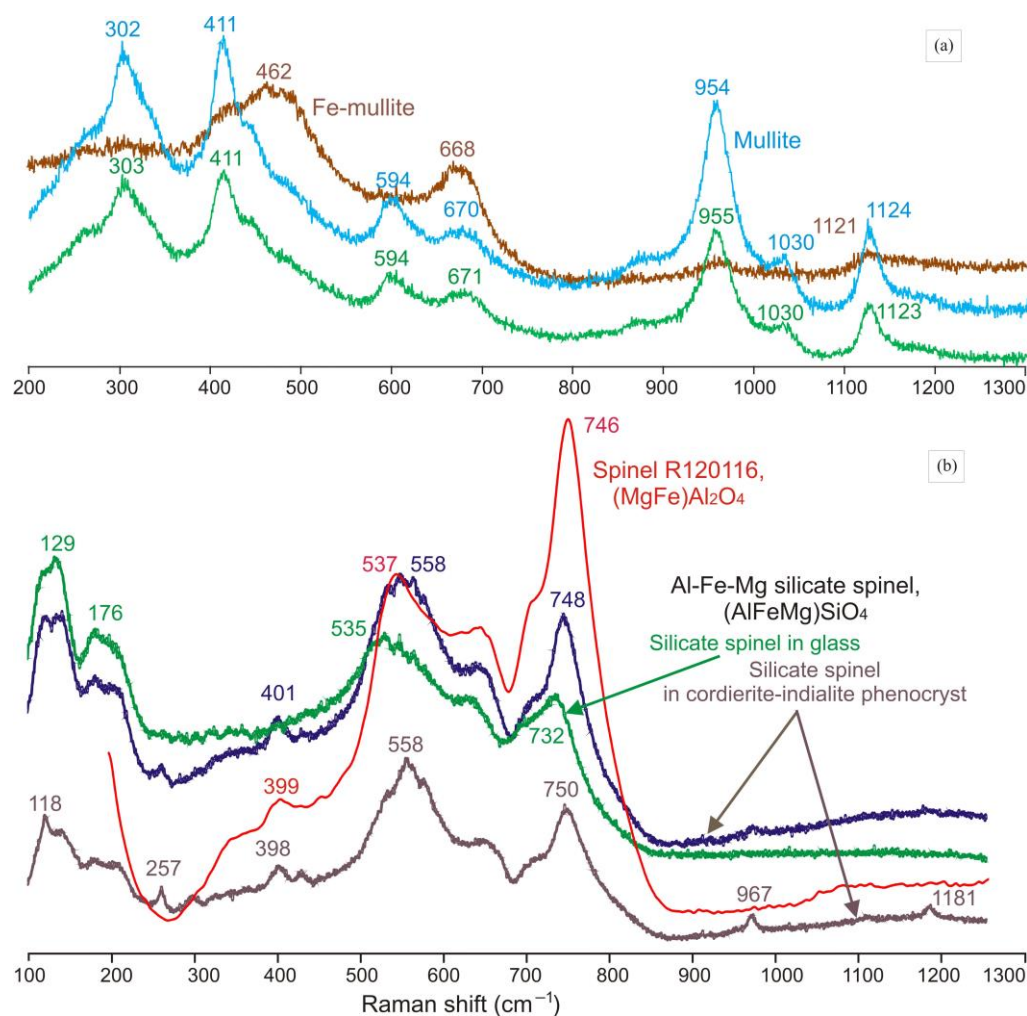


Figure 8. Raman spectra of mullite, Fe-mullite (a) from cristobalite clinker, sample MN-1405 and anhydrous Al-Fe silicate, presumably, new spinel-group mineral (b) from clinker sample MN-1129, compared to reference spinel (R120116) from RRUFF database.

Fe^{3+} can substitute for Al^{3+} in the mullite structure. Mullite in all clinker samples contains 1–3 wt% Fe_2O_3 tot. According to experimental data [23], the contents of Fe_2O_3 inferred from the empirical Fe^{3+} solubility plot decrease progressively from 10.5 to 2.5 wt% as the temperature increases from 1300 to 1670°C , while the highest Fe_2O_3 reach 12.5 wt% or 6 mol%. In the most ferroan grains of mullite, the absorption band of about 600 cm^{-1} associated with stretching vibrations of AlO_6 [22] is poorly pronounced, though typical mullite peaks at $\sim 460, 670$, and 1025 cm^{-1} are present (Figure 8a). Judging by the experimental evidence [23] and the Raman spectra features, some Fe-rich silicate grains can be identified as Fe-mullite.

3.3.3. Al-Fe-Mg Silicate Spinel

Together with mullite and Fe-mullite in the clinker matrix, there are also numerous areas containing microliths up to 2–3 μm in size in the maximum cross-section and submicron ($<1\ \mu\text{m}$) grains of silicate minerals (Figure 2) with large variations in contents of Al (40–55 wt% Al_2O_3), Fe (13–24 wt% FeO), and Mg (up to 12 wt% MgO). In the cristobalite clinker from the Khamaryn–Khural–Khiid CM complex, some needle-shaped microliths and grains (bright phases in BSE images, Figures 2 and 5) of these minerals contain 20–24 wt% FeO, and in the clinker sample MN-1129 from the Nyalga CM complex the content of MgO in them is 8–12 wt%.

Numerous inclusions of Al-Fe-Mg silicates are also found in the studied cordierite–indialite phenocryst and in the surrounding clinker glass (Figure 5). The most ferroan silicates have a low Mg content and are close in composition to staurolite $\text{Fe}^{2+}_2\text{Al}_9(\text{SiAl})_4\text{O}_{20}(\text{O},\text{OH})_4$. However, according to the Raman spectra, there is no hydroxyl in these Al-Fe silicates and its absorption bands completely correspond to spinel (MgFe^{2+}) Al_2O_4 from RRUFF database (Figure 8b).

Fe-Mg silicate spinels with an ideal crystal chemical formula ($\text{Mg}_x\text{Fe}_{1-x}$) $_2\text{SiO}_4$ were previously synthesized [24]. Their natural analogs are the ahrensite, Fe_2SiO_4 [25] and ringwoodite, (MgFe^{2+}) $_2\text{SiO}_4$ [26]. The $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_4$ or $\text{Al}_3\text{Si}_3\text{O}_{12}$ phase with a spinel structure is known to be formed due to thermal transformation of kaolinite and illite (e.g., at coal combustion, after [27]). Based on Raman spectra and SEM-EDS data, grains of anhydrous silicates with large variations in Al, Fe, and Mg contents have a spinel structure and, probably, the stoichiometric formula ($\text{AlFe}^{2+}\text{Mg}$) SiO_4 , which does not correspond to any compositions of spinel-group minerals approved by the International Mineralogical Association (IMA) [28].

3.3.4. Quartz and Silica Polymorphs

Remnant grains (partly melted or dissolved) of detrital quartz are found in all varieties of CM rocks, but most of these are found in clinkers (Figure 2a,b). In the clinker and ferroan paralavas of the Khamaryn–Khural–Khiid CM complex, silica polymorphs were diagnosed: rock-forming α -cristobalite and α -tridymite. Detrital quartz grains commonly lack impurities resolvable by SEM-EDS. Al_2O_3 in some cristobalite microliths is up to 1 wt%, whereas tridymite contains 2–5 wt% Al_2O_3 , 1–3 wt% FeO, and within 0.4 wt% K_2O .

Let us note a characteristic feature of many large grains of detrital quartz in the matrix of tridymite–sekaninaite paralava (samples MN-1363 and MN-1368). Such quartz grains contain thin cristobalite veinlets and are surrounded by a rim (10–50 μm) consisting of α -cristobalite and glass similar in composition to quartz ($\text{SiO}_2 > 90\ \text{wt}\%$), which is replaced by an outer α -tridymite rim (Figure 4).

3.3.5. Olivine-Group Minerals

Olivines, less abundant than the rock-forming phases in melilite–nepheline paralava, were described in detail in our previous publications [1–3,5]. Mg-Fe olivine in the analyzed CM rocks has a fayalitic composition with a moderate amount of Mg (0.2–0.3 apfu) and minor Mn (0.05–0.25 apfu) contents. Fayalite is enriched in Mn (~ 0.3 apfu, up to 10 wt% MnO) in tridymite–sekaninaite paralava sample MN-1368. Olivine in cristobalite–fayalite paralava sample MN-1370 contains less Mn (0.1–0.2 apfu, 2–3 wt% MnO). In paralava samples MN-1368 and MN-1370, fayalite contains 1–3 wt% P_2O_5 , and the highest phosphorus concentration (up to 5 wt% P_2O_5) has fayalite in sample MN-1370.

P-bearing olivine with $>2\ \text{wt}\%$ P_2O_5 occurs very rarely in terrestrial rocks and in meteorites [29]. The highest P_2O_5 contents of up to 23 wt% were measured in Mg-Fe olivine from CM rocks produced by the partial melting of gneiss [30].

3.3.6. Pyroxene-Group Minerals

Pyroxenes occur in all varieties of CM rocks as up to 0.5 mm euhedral phenocrysts and microliths or, less often, as elongate dendritic crystals and grains of various shapes.

Clinopyroxene, one of main rock-forming minerals in melilite–nepheline paralava, exists as zoned phenocrysts with Al and Mg decreasing while Fe increase rimward. The mineral plots above the diopside and hedenbergite fields in the Wo , $CaSiO_3$ – En , $Mg_2Si_2O_6$ – Fs , $Fe_2Si_2O_6$ diagram, due to the presence of Al_{VI} (up to 49 mol% kushiroite end-member $CaAl_2SiO_6$) in Mg-rich core zones with $Mg\#$, $Mg/(Mg + Fe^{2+} + Fe^{3+}) = 0.5–0.8$ [1–3,6].

Orthopyroxene, an accessory in cristobalite clinker and a minor phase in tridymite–sekaninaite paralava, was identified as ferrosilite from SEM-EDS and Raman spectra. Its identification by XRD is difficult because of modest pyroxene amounts in the rocks, but ferrosilite and clinoferrosilite are well discriminated in Raman spectra, which are thus suitable for local detection of phases. Ferrosilite contains 76–89 mol% of the Fs end-member and various impurities: <10 wt% Al_2O_3 , <8 wt% MnO , <1 wt% TiO_2 , <0.8 wt% CaO , and <2 wt% P_2O_5 . Ferrosilite in paralava sample MN-1368 shows the highest Mn enrichment: 6–8 wt% MnO , 0.2–0.3 apfu Mn.

4. Discussion

The formation of baked and melted rocks of the Mongolian CM complexes was caused by multistage underground wild coal fires in the Early Cretaceous sedimentary strata, which occurred here at different times, from the Quaternary period to the present day [1–4]. Partial melting of Fe-enriched pelitic sediments (mudstone, siltstone, and silty sandstone) led to the formation of clinkers and ferroan paralavas with rock-forming cordierite-group minerals, mullite, Fe-mullite, Al-Fe-Mg silicate spinel, cristobalite, tridymite, fayalite, and other phases in different relative percentages.

The large diversity of mineral assemblages in the CM rocks is due to the heterogeneous protolith lithology and local conditions for the multistage combustion metamorphic processes [1–6]. Melilite–nepheline paralavas, the most widespread variety in the Nyalga and Khamaryn–Khural–Khiid CM complexes, results from thermal alteration and the melting of marly limestone. High-temperature low-pressure combustion metamorphism of the sedimentary protoliths produced a mineral assemblage of gehlenite and Al-clinopyroxene (kushiroite end-member enriched) in the marly limestone [3,4,6].

It was previously shown [4] that the underground wild coal fires heated the overburden carbonate–silicate sedimentary strata from below at a relatively high partial pressure of CO_2 in unique P – T conditions, without thermal decomposition of calcite into CaO and CO_2 . Incongruent melting, which involved thermally modified silicate (pelitic) matter of the marly limestone, occurred within the stability field of calcite at a CO_2 partial pressure that precluded its decomposition. The suggested qualitative petrological model implies melting under the conditions of $T > 1100$ °C, $P_{CO_2} < 40$ bar for K-Na feldspar and $T > 1250$ °C, $P_{CO_2} > 40$ bar for calcite and other refractory minerals (gehlenite, Al-clinopyroxene, etc.). The melting process led to the formation of immiscible melts: a carbonate (non-stoichiometric $CaCO_3 + CaO$ or stoichiometric calcitic) and several compositionally diverse silicate melts. The coalescence of silicate melts was followed by formation of a silica-undersaturated Ca-rich melt parent to melilite–nepheline paralava.

4.1. Melting Processes of Fe-Enriched Pelitic Rocks

The processes of baking, partial and full melting of pelitic rocks leading to changes in mineral assemblages can be reconstructed with regard to the crystallization features and phase transitions of mullite, silica polymorphs, and cordierite-group minerals, both in natural and experimental systems. Pelitic and metapelitic rocks can melt partially at the P – T parameters of the spurrite–merwinite facies comparable to combustion metamorphism [31]. Eutectic and cotectic melts appear on grain boundaries of quartz, feldspar, micas, and Al-Mg-Fe-rich phyllosilicates. The incongruent melting of pelitic rocks often remains incomplete, and glasses retain remnant fused grains of primary minerals. In the process of clinker formation, fine amorphous matter melts at temperatures lower than those required for coarse grains of silicates.

It has been experimentally established that during the thermal alteration, the partial and full melting of pelitic sediments and the formation of clinkers in CM complexes occurs in the following temperature ranges, according to [8]: (1) dehydration–dehydroxylation and related amorphization of the pelitic matter at 600–700 °C; (2) sintering with limited crystallization of anhydrous oxides and silicates in solid-state reactions at 700–870 °C; (3) local melting, formation of K-rich aluminosilicate eutectic melts, and crystallization of cordierite-group minerals, mullite, spinels, and plagioclase at 870–1200 °C.

4.1.1. Nonequilibrium Conditions Formation of Clinkers

Mullite, Fe-mullite, and Al-Fe-Mg silicate spinel in the Khamaryn–Khural–Khiid cristobalite clinker and in the Nyalga clinkers appear as clusters of multiple acicular microliths and grains of micron and submicron sizes in many matrix zones in different volumetric proportions (Figures 2 and 5). According to [8,31], SEM-EDS, XRD, and Raman spectra, we assume that the mineral association of mullite, Fe-mullite, and Al-Fe-Mg silicate spinel in clinkers of CM complexes crystallized, starting from the early stage of CM transformations of pelitic rocks during dehydration–dehydroxylation reactions and the amorphization of phyllosilicates [32]. Large-scale crystallization of mullite occurs at $T > 850$ °C, as in the case of high-temperature silicate ceramics [8]. Fe-mullite and silicate spinel of variable compositions $(\text{AlFe}^{2+}\text{Mg})_2\text{SiO}_4$ may have been formed from thermal destruction of Al-Mg-Fe-rich phyllosilicates, ‘meta-kaolinite’, and ‘meta-illite’ in thermally modified Fe-enriched pelitic rocks at $T > 900$ °C, after [27,33]. Apparently, the temperature range of 850–900 °C is the minimum for the large-scale crystallization of the above minerals in K-rich peraluminous melts during clinkers formation.

Raman spectroscopy and SEM-EDS data revealed hexagonal (indialite and ferroindialite) and orthorhombic (cordierite and sekaninaite) cordierite-group minerals in clinkers, as well as coexisting hexagonal and orthorhombic varieties in some cristobalite clinker and in clinker xenolith from melilite–nepheline paralava (Figures 2, 5 and 6, Table S1). Till recently, the description of ferroindialite was limited to a mudstone xenolith from basalt found in Eifel, Germany [34], and Nyalga CM rocks [2].

All cordierite-group minerals in CM rocks contain potassium from 0.03 to 0.19 apfu (0.2–1.4 wt% K_2O). The highest K contents are found in microliths and outer zones (rims) of phenocrysts, which crystallize in K-rich peraluminous melts. Thus, the most-potassium mineral in the Nyalga clinker sample MN-1129 is Fe-rich indialite (Figure 5), and in the Khamaryn–Khural–Khiid cristobalite clinker it is cordierite–sekaninaite or indialite–ferroindialite (Figures 2 and 7b,d, Table S1). From this, we conclude that the isomorphic impurity of potassium in cordierite-group minerals does not correlate with their crystal structure—hexagonal or orthorhombic.

According to experimental evidence, hexagonal indialite can crystallize from cordieritic melt at $T > 1450$ °C (stable) or between 1050 °C and 1445 °C, for the metastable variety [18], whereas stable orthorhombic cordierite–sekaninaite crystallizes at $T < 1000$ °C [21]. The presence of indialite and ferroindialite in cristobalite clinker indicates that the maximum partial melting temperature of pelitic rocks exceeded 1050 °C, but the crystallization of cordierite and sekaninaite was possible at $T < 1000$ °C.

All clinker samples enclose remnant grains of detrital quartz, rarely fused or partly dissolved, as well as in the Khamaryn–Khural–Khiid cristobalite clinker ubiquitous rock-forming cristobalite in elongate grains or in intergrowths with ferroindialite, sekaninaite, or plagioclase (Figure 2). Hexagonal β -tridymite is considered to be an equilibrium phase growing from partial melts of pelitic or metapelitic material, whereas metastable cubic β -cristobalite crystallizes in the stability field of β -tridymite [31,35]. In the range of 1300–1400 °C, detrital quartz grains in clinker remain unaltered, β -cristobalite appears as a metastable phase, and β -tridymite crystallizes from high-silica K-rich melts at $T > 870$ °C [8]. Therefore, the large-scale crystallization of cristobalite in the Khamaryn–Khural–Khiid clinker can hardly be evidence of pelitic rocks melting in the stability field of β -cristobalite. On the other hand, the absence of tridymite and the presence of numerous fused quartz

grains in cristobalite clinker indicate that the Khamaryn–Khural–Khiid pelitic rocks may have been heated to $T > 1470$ °C.

Possible evolutionary paths in the clinker mineralogy can be traced in phase diagrams of the liquidus surface for the Al_2O_3 –FeO– Fe_2O_3 – SiO_2 major-oxide system, taking into account experimental data and thermodynamic modeling, after [36]. The Al_2O_3 –FeO– SiO_2 phase diagram (Figure 9a, Path 1) shows that the equilibrium crystallization of melt corresponding to an average cristobalite clinker composition begins in the field of mullite (1650–1600 °C) and is followed by cotectic formation of β -cristobalite, β -tridymite, and Fe-cordierite. The latter forms within a small site of the liquidus surface, in the temperature range from 1224 °C to the eutectic point at 1078 °C. The field of Fe-cordierite in this diagram rather corresponds to the field of ferroindialite or metastable sekaninaite, because stable cordierite cannot crystallize at $T > 1050$ °C [18].

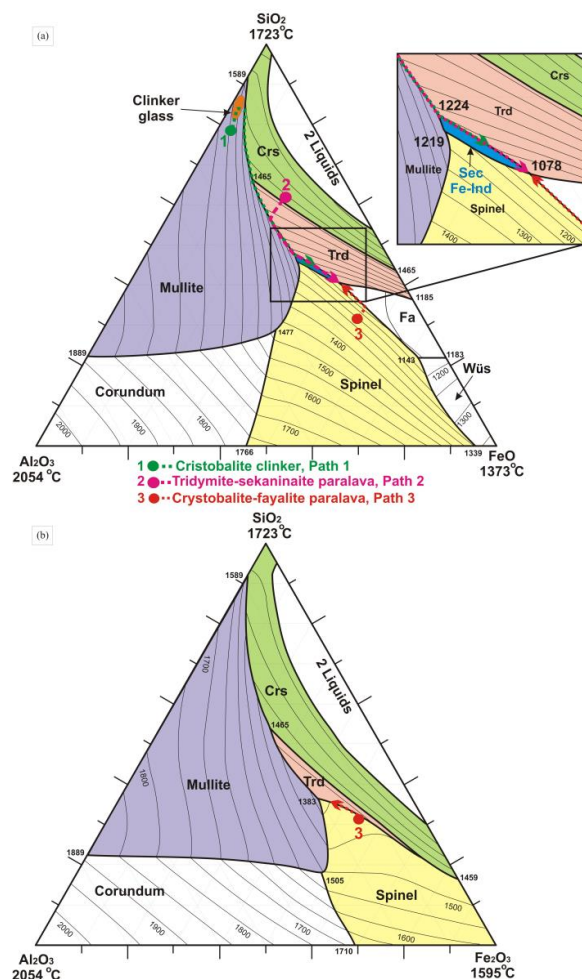


Figure 9. Liquidus surface in the Al_2O_3 –FeO– Fe_2O_3 – SiO_2 major-oxide system according to experimental data and thermodynamic optimization, after [36]. Oxide phases are in equilibrium with metallic iron (a), and at $P(\text{O}_2) = 0.21$ atm (b). Temperatures at the corners correspond to melting of oxides; temperatures along cotectic lines and at eutectic points correspond to phase transitions. Sec = sekaninaite, Fe-Ind = ferroindialite, Wüs = wüstite, Fa = fayalite, Crs = cristobalite, Trd = tridymite.

The temperature range of ferroindialite crystallization obtained from the phase diagram agrees with evidence from [37] that Fe, and K-bearing indialite in mudstone xenoliths entrapped by the lava of Vesuvium crystallized at ~ 1200 °C. However, the equilibrium crystallization of Khamaryn–Khural–Khiid clinker (Figure 9a, Path 1) is inconsistent with the absence of tridymite in its phase composition, as well as with mullite crystallization

at $T > 700\text{--}870\text{ }^{\circ}\text{C}$, after [8]. Apparently, the overburden pelitic rocks above the burning coal layers became heated to $>1050\text{ }^{\circ}\text{C}$ (judging by the crystallization conditions for cordierite-group minerals) or locally to $>1300\text{ }^{\circ}\text{C}$ (the temperature range of detrital quartz melting) and, possibly, even to $>1470\text{ }^{\circ}\text{C}$ (the stability field of β -cristobalite). Intergrowths of β -cristobalite (possibly, metastable in the stability field of β -tridymite) with indialite–ferroindialite, cordierite–sekaninaite, or plagioclase crystallized in the most strongly molten zones of the clinker matrix, from a high-silica K-rich and Fe-enriched peraluminous melt (Figure 2). Hexagonal indialite and ferroindialite retained their structure in some fragments of the CM rocks, possibly, due to the very fast cooling of local zones of sedimentary strata and the quenching of high-temperature peraluminous melt.

4.1.2. Formation Conditions of Ferroan Paralavas

The mineral assemblages including K-bearing sekaninaite, tridymite, Ti-magnetite, pyroxene (clinoferrosilite or ferrosilite), and high-silica K-rich aluminosilicate glass, as in the Khamaryn–Khural–Khiid tridymite–sekaninaite paralava with spinifex-like matrix texture, were reported from many CM complexes [8,10,38,39]. Samples MN-1363 and MN-1368 of such paralava have well-defined crystalline structures (Figure 3a,d), and their mineral assemblages may have formed from a Fe-rich silicate melt, possibly, in quasi-equilibrium conditions. In the phase diagram (Figure 9a, Path 2), the formation of such paralava starts with cristobalite near the field of tridymite and, then, continues within the latter cotectically with mullite, to finally reach the eutectic crystallization of fayalite. In the mineral assemblage of the tridymite–sekaninaite paralava samples, the final crystallization stage of the matrix produced tridymite (possibly, paramorph after β -cristobalite), ferrosilite, and glass from small zones of residual K-rich peraluminous melt. The partial melting of detrital quartz grains with cristobalite veinlets in this paralava (Figure 4) may have started in the stability field of β -cristobalite.

Cristobalite–fayalite paralava (sample MN-1370) likewise crystallized from an Fe-rich silicate melt, but at higher oxygen fugacity than in the case of tridymite–sekaninaite paralava. In the $\text{Al}_2\text{O}_3\text{--FeO--SiO}_2$ major-oxide system (Figure 9a, Path 3), the crystallization of parental paralava melt began in the field of spinel at $1250\text{--}1200\text{ }^{\circ}\text{C}$ and continued cotectically with fayalite. The sample lacks cordierite-group minerals, probably due to the high degree of oxidation of iron in the melt. According to the phase diagram of the $\text{Al}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--SiO}_2$ major-oxide system, after spinel, tridymite crystallizes along the cotectic near the cristobalite field (Figure 9a, Path 3). In the real crystallization sequence, spinel-group minerals (Al-magnetite, Al-spinel) were also the first liquidus phases and were followed by fayalite, while cristobalite and K-Na feldspar crystallized in the interstices between matrix minerals (Figure 3e,f).

Ferrous paralavas formed after the complete melting of Fe-enriched pelitic rocks during the rapid crystallization of Fe-rich silicate melts, as indicated by the spinifex-like textures of the matrix (Figure 3a,b,e,f). The least high-temperature ($<1250\text{ }^{\circ}\text{C}$) and most-oxidizing conditions were observed during the crystallization of Fe-rich silicate melts parental for cristobalite–fayalite paralava. Such conditions are common to underground coal fires when atmospheric oxygen can easily access the zone of ignition through fractured overburden sedimentary strata.

5. Conclusions

Melted rocks of the Mongolian CM complexes with various mineral-phase assemblages were formed as a result of multistage wild underground coal fires in the Early Cretaceous sedimentary strata. Clinkers, tridymite–sekaninaite, and cristobalite–fayalite ferroan paralavas were produced by the partial melting of Fe-enriched pelitic rocks (mudstone, siltstone, and silty sandstone) over a large temperature range.

According to XRD, Raman spectroscopy, and SEM-EDS data, cordierite, sekaninaite, indialite, ferroindialite, silica polymorphs, mullite, Fe-mullite, anhydrous Al-Fe-Mg silicate spinel (presumably new minerals), and other phases were identified. It was established

that isomorphic impurity of potassium in the cordierite-group minerals does not correlate with their crystal structure (hexagonal or orthorhombic).

Mullite, Fe-mullite, and Al-Fe-Mg silicate spinel in clinkers were formed in the process of dehydration–dehydroxylation and the incongruent melting of finely dispersed Fe-enriched pelitic matter (Al-Mg-Fe-rich phyllosilicates, ‘meta-kaolinite’, and ‘meta-illite’). Large-scale crystallization of these minerals in the clinker K-rich peraluminous melts presumably occurred in the temperature range above 850–900 °C.

From experimental data on the crystallization conditions of hexagonal and orthorhombic phases of cordierite-group minerals in clinkers, it follows that the partial melting temperature of pelitic rocks exceeded 1050 °C, and crystallization of cordierite–sekaninaite occurred at a temperature range < 1000 °C. The subsurface combustion of coal layers heated the overburden pelitic rocks to $T > 1050$ °C or locally till the melting point of quartz ($T > 1300$ °C) and, possibly, till the stability field of stable β -cristobalite ($T > 1470$ °C). Indialite and ferroindialite found in the clinkers matrix and in clinker xenoliths from paralavas retained their hexagonal structure, probably due to the very rapid cooling and glass transition (quenching) of K-rich peraluminous melts formed under nonequilibrium conditions of incongruent melting of Fe-enriched pelitic rocks.

Tridymite–sekaninaite and cristobalite–fayalite ferrous paralavas were formed during the rapid crystallization of Fe-rich silicate melts under various redox conditions. From the analysis of liquidus surface in the Al_2O_3 –FeO–Fe $_2\text{O}_3$ –SiO $_2$ major-oxide system, it follows that the least high-temperature ($T < 1250$ °C) and most-oxidizing conditions occurred during the crystallization of mineral assemblages in the most-enriched iron silicate melt parental for cristobalite–fayalite paralava.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/geosciences13120377/s1>, Table S1: Mineral chemistry and crystal chemical formulas of cordierite-group minerals.

Author Contributions: Conceptualization and investigation, I.S.P.; field sampling, writing, review, and editing, all authors; visualization, E.A.S. All authors have read and agreed to the published version of the manuscript.

Funding: The study was funded by grant 23-27-00031 from the Russian Science Foundation (RSF).

Data Availability Statement: Data are available in the Table S1 (Supplementary Materials).

Acknowledgments: We appreciate the collaboration of our colleagues in analytical work: A.N. Sapozhnikov (IGC, Irkutsk) for XRD analysis, Yu. D. Shcherbakov (IGC, Irkutsk), and A.G. Chueshova (IGC, Irkutsk) and E.A. Khromova (GIN, Ulan-Ude) for SEM-EDS measurements.

Conflicts of Interest: The authors declare no conflict of interest.

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