

Role of water in the origin of podiform chromitite deposits

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Received 15 November 2001; received in revised form 10 April 2002; accepted 24 July 2002

Abstract

We report experiments in basalt oversaturated with water to duplicate the nodular ore textures of podiform chromitite ores. In immiscible basalt–water systems saturated with olivine and chromite, olivine will reside in the melt while chromite will collect in the fluid phase. Fractionation is physical and is driven by differential wetting properties of melt and fluid against silicate and oxide surfaces. There is no need to suppress olivine from the liquidus of a primitive basaltic melt as suggested by Irvine [Irvine, T.N., *Geology* 5 (1977) 273–277], to achieve chromite accumulations as observed in natural podiform ore deposits. The results imply that podiform chromitite ores will form where a primitive olivine–chromite-saturated mantle melt is sufficiently water-rich to exsolve a fluid phase during passage through the uppermost mantle. The most likely geodynamic environment for podiform chromite mineralization to take place is a supra-subduction zone setting.

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Keywords: podiform deposits; chromitite; platinum group; ophiolite; seawater; saturation

1. Introduction

Podiform chromitites are genetically interesting and economically important, yet poorly understood. According to present knowledge, podiform chromitites are confined to oceanic crustal sections of ophiolite complexes and usually situated in lithostratigraphic positions near the petrologic MOHO [2–4]. Most podiform chromitite occurrences appear to be associated with dunite melt channels in harzburgite or lherzolite peridotite [5,6]. According to Fe–Mg exchange temperatures [7,8] of bulk chromite and coexisting bulk silicate

mantle dunite or harzburgite material (1150–1200°C), they are undoubtedly magmatic in origin.

Many questions relating to the origin of podiform chromitites are still unanswered. For example, how is the great enrichment of chromium being accomplished? Primitive mantle melts typically have chromium concentrations of around 200–500 ppm whereas economically viable chromite deposits contain around 30% Cr in bulk ore. A basic requirement for this enrichment is that olivine and chromite become physically separated at magmatic temperature, in primitive melts that are normally saturated with both olivine and chromite [1].

Perhaps the ore textures of podiform chromitites offer an explanation for the enrichment process [9,10]. Many undeformed chromitite pods

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contain nodular ores in which polycrystalline, rounded aggregates of chromite crystals are set in a dunite matrix (Fig. 1). The mirror image, i.e. dunite orbicules set in chromite matrix, is also observed although apparently rarer [10,11]. The potential genetic significance of these unique textures is often ignored or attributed to physical processes possible in any magmatic system, such as snow-balling of chromite phenocrysts in turbulent melt or disruption of plastic chromitite layers [2,11,12]. In our opinion, their importance for understanding the chromite enrichment process has been underestimated.

Another unsolved question relates to the geotectonic setting in which podiform chromitite ores may form [3,13,14]. Schiano et al. [14] addressed this problem by analyzing homogenized hydrous silicate (sodic amphibole and phlogopite-rich) inclusions in chromite from the Oman ophiolite. They found a negative Nb anomaly in the trace element patterns and concluded that the Oman ophiolite formed in a fossil back-arc setting. Many obvious questions, however, were left unanswered by this study [15]: Are the hydrous silicate inclusions in chromite trapped equilibrium melts? Is it realistic to assume that primitive melts with chromite on the liquidus have H₂O contents sufficient to stabilize amphibole and phlogopite at a temperature where chromite crystallizes? Does

water play a role in the enrichment of chromite in ophiolitic upper mantle [16]?

This paper reports novel fractionation experiments in a conjugate basalt–water system to study the fractionation of olivine and chromite between silicate melt and a water-rich fluid phase. The study was motivated by the unique nodular ore textures (Fig. 1). It extends an experimental study by Ballhaus [9] in an immiscible silicate model system to a more natural bulk composition. We show that in immiscible basalt–water systems, chromite and olivine are strongly fractionated from each other. Chromite partitions into the exsolved fluid whereas olivine (and possibly other silicate phases) stays in the silicate melt. Fractionation occurs by differential wetting properties of fluid and melt against silicate and oxide surfaces. The enrichment process identified is equivalent to the industrial process known as ‘flotation’.

2. Experimental details and results

The starting mixture was a picritic melt composition [17] synthesized from oxides and doped with excess water. In addition, we added 2% (Mg,Fe)Cr₂O₄ oxide component, calculated to be in Fe–Mg exchange equilibrium with Fo₉₀ at 1200°C [8]. All experiments were done in Pt cap-

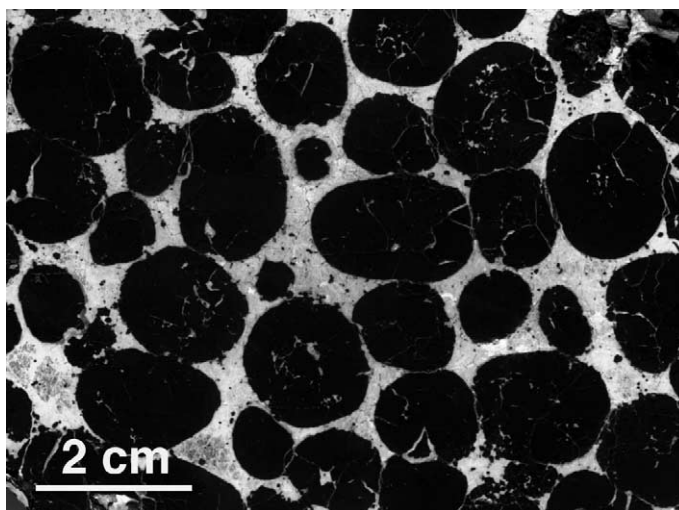


Fig. 1. Image of nodular podiform chromite ore from Cyprus. Dark roundish nodules of polycrystalline aggregates of magnesiochromite set in a formerly dunitic matrix, now hydrated and oxidized to chrysotile, talc, tremolite, and magnetite.

sules in a piston cylinder press. Temperature ranged from 1150 to 1200°C. To trigger fluid exsolution, all runs were initially compressed to 1.5 GPa for several minutes, then slowly decompressed at run temperature to 0.4 GPa run pressure. Run times ranged from 15 min to up to 72 h. With few exceptions (see below) runs were quenched by turning off the power supply.

Transmitted light and backscatter images of run products are compiled in Fig. 2. After quenching, silicate glass coexisted with chromite and a separate fluid phase, and lower temperature (1150°C) runs with olivine, chromite, and fluid. We note marked fractionation of olivine and chromite between fluid and silicate melt. All chromite microphenocrysts were found concentrated in exsolved fluid pools while olivine remained in silicate glass, well separated from chromite. Collection is so efficient that even in the experiment with the shortest run time (15 min), every single chromite microlith was found totally wetted by the fluid phase.

3. Chromite concentration processes

With regard to the chromite concentration process, we distinguish between small-scale fractionation of chromite into the fluid phase and large-scale concentration in nature to mineable ore bodies. In experiment, chromite concentration is controlled by surface processes. In conjugate silicate melt-water systems, crystal faces of oxides are wetted better by water-rich fluid than by silicate melt [18], probably reflecting differences in crystal-fluid and crystal-melt interfacial energy. The opposite is true for silicate minerals; in all our experiments where chromite coexisted with olivine (as well as fluid and silicate melt), olivines were found wetted exclusively by silicate melt. Fluid pools were found olivine-free.

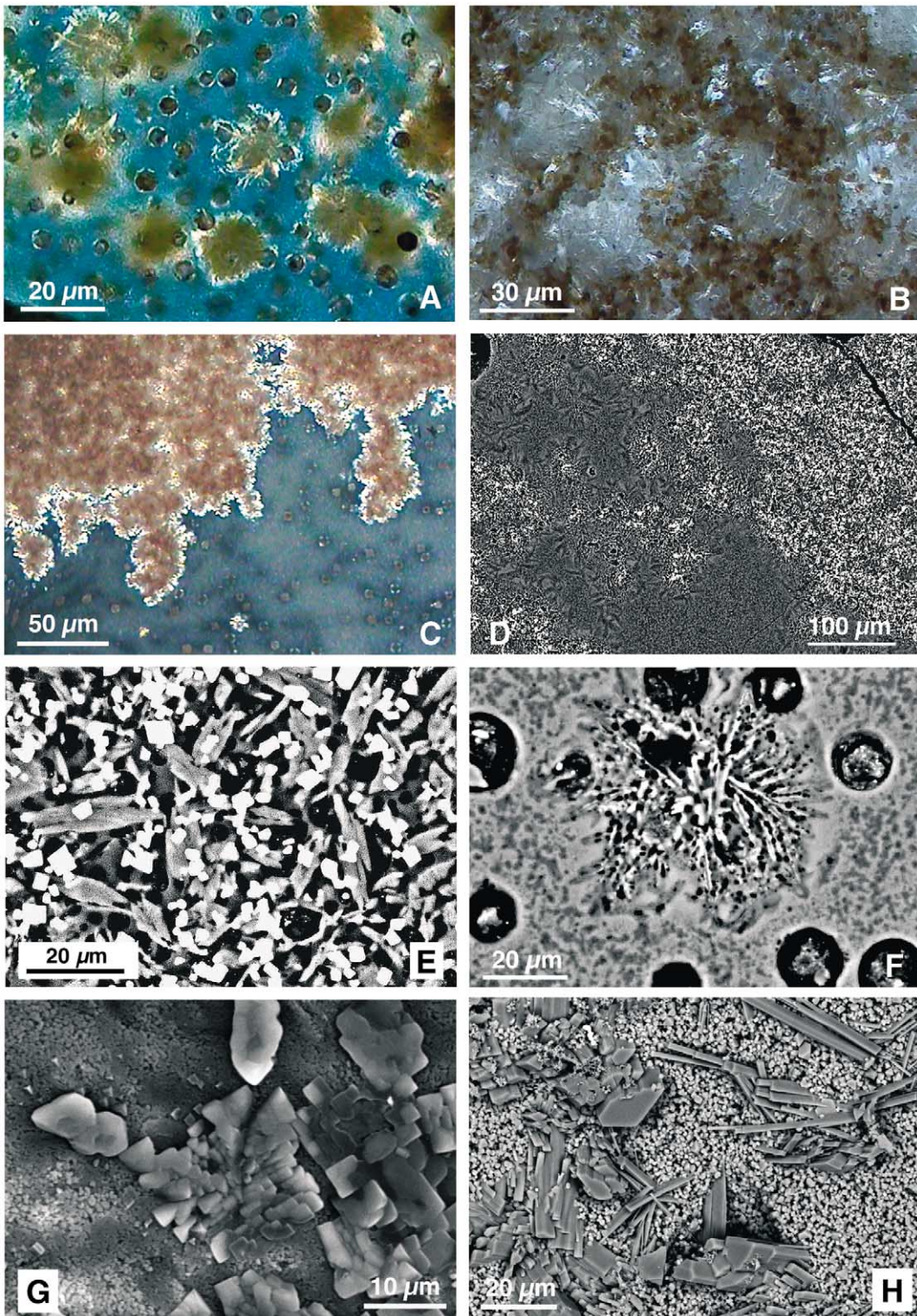
Time series experiments, illustrated in Fig. 2A–C, demonstrate that chromite fractionation occurs during the experiment and not during quenching. With increasing run time, chromite-laden fluid bubbles first coalesce to larger pools, then migrate toward the container walls, and finally collect in the upper part of the experimental capsule, all

within a few hours. There is also fluid exsolution during quenching, but quench fluid bubbles are easily distinguished from equilibrium fluid pools by being smaller, spherical, evenly distributed throughout the silicate glass, and devoid of trapped chromite microliths (Fig. 2F).

The large-scale concentration of chromite to ore bodies is driven by density contrasts between chromite-laden fluid pools and silicate melt, following Stoke's law. Collection of chromite will commence as soon as a decompressing, water-rich melt exsolves a fluid phase. Given the affinity of water-rich fluid to oxide surfaces we propose that an exsolving fluid phase will tend to use as nucleation points chromite microphenocrysts dispersed in the melt. With time in a convecting magma body, individual fluid bubbles will come into contact and will coalesce to larger fluid pools (Fig. 2B). We assume that the surface tension of a fluid pool is sufficient to keep dispersed chromite crystals inside the fluid once chromite is trapped, so in calculating density relations between fluid bubbles and basaltic melt, chromite-laden fluid pools are treated as an entity.

The density calculation then is straightforward. The minimum density of the fluid at 1200°C and 0.2 GPa, calculated using the Redlich-Kwong equation of Holloway [19], is around 275 kg m⁻³, ignoring the density contribution from the solute. The density of chromite is ~4500 kg m⁻³ [20] and that of an average basaltic melt with 4% dissolved H₂O is ~2520 kg m⁻³ [21,22]. Hence, a fluid bubble with < 50% dispersed chromite will be able to rise, and a bubble with > 50% chromite will sink relative to the basaltic melt (Fig. 3).

The nodular texture is believed to be a secondary phenomenon (Fig. 4). Following nucleation, a fluid bubble initially has so little chromite that it will be buoyant relative to the silicate melt. As such, it will rise up in the magma conduit. Near the top of the chamber, bubbles will concentrate and eventually coalesce to larger fluid pools. Inside their fluid substrate, chromite crystals are free to settle and to accumulate at the bottom of coalesced fluid pools, until local chromite concentrations exceed the density of the underlying and supporting silicate melt sheet. In our Fig. 4, this situation produces small 'downspouts', i.e. down-



ward-directed, chromite-laden plumes that disrupt and reshape to droplets as they sink, to minimize their surface to volume ratio against the silicate melt. It is essential that the surface tension of the fluid wetting the dispersed chromite grains be sufficient to minimize disintegration of nodules while they sink. The average size of a chromite nodule will be a function of density and viscosity contrasts between silicate melt and chromite-laden nodules, relative surface tensions, and sinking velocity, as well as reflecting the convective regime of the silicate melt body through which the nodule sinks.

The experiments also account for other textural types of podiform chromite ore. For example, in early stages an exsolving fluid forms a network of chromite-laden channels in silicate melt (cf. Fig. 2B). Preserved *in statu nascendi* it would solidify to chromite stringers in silicate matrix. Larger experimental fluid pools often contain spherical silicate melt globules, and if these are preserved by rapid solidification they could give rise to orbicular (ring-shaped) ore textures [10,11]. In most instances, however, primary textures are obliterated by coalescence and annealing, producing the most ubiquitous type of massive chromite ore.

4. Hydrous silicate inclusions in chromite

Many discordant podiform chromites contain parasitic amphibole and phlogopite inclusions [23–27], and occasionally hydrous saline fluid inclusions [28]. All these inclusions occur as negative crystal-shaped octahedra. Inclusion morphol-

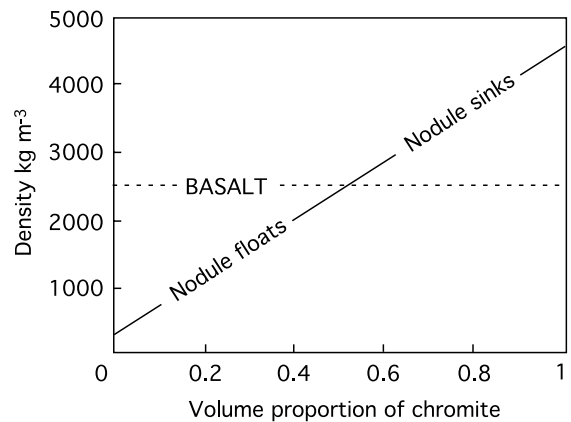


Fig. 3. Density relations between aqueous fluid, chromite, and hydrous basaltic melt at 0.2 GPa and 1200°C, corresponding to the lithostatic pressure near the petrologic MOHO in ophiolite complexes, the position where most podiform chromite ores are situated. For assumptions and data sources see text.

ogy is imposed by the cubic symmetry of the chromite host. Judging from their shapes they were trapped during chromite growth. Schiano et al. [14] homogenized hydrous silicate inclusions and contended that they represent a primary melt component from which chromite crystallizes. Johan and coworkers [26,27] took the hydrous inclusions as evidence that podiform chromite ore is hydrothermal in origin, in the sense that chromium was transported and enriched to the ore site via a fluid phase.

Fig. 2G,H shows the result of an isobaric cooling experiment cooled with $1^{\circ} \text{min}^{-1}$ from 1200 to 800°C, then quenched. The experiment was carried out to test which phases a magmatic fluid, in

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Fig. 2. Transmitted light and backscatter images of run products in conjugate picrite-fluid systems. (A) Incipient exsolution of fluid after 15 min run time (1200°C, 0.4 GPa) in transmitted light; silicate glass blueish, exsolved fluid brownish due to chromite microliths. The large rounded bubbles are equilibrium fluid pools, the small ($< 5 \mu\text{m}$) bubbles are quench fluid. (B) Formation of an interconnected fluid network after 1 h run time at 1200°C and 0.4 GPa, transmitted light; chromite is brownish, silicate material quenched out of the fluid is whitish. (C) Discrete fluid pools with chromite (brownish) coexisting with silicate glass, after 24 h at 1200°C and 0.4 GPa, transmitted light; the small bubbles in glass are quench fluid. (D) Backscatter image of bright chromite-rich fluid pool coexisting with darker silicate glass rich in quench phases (1200°C, 0.4 GPa after 24 h). Silicate glass (gray, with quench olivine) coexisting with a fluid pool rich in chromite (bright). (E) Backscatter image of chromite (white) coexisting with feathery quench silicates in fluid pool (1200°C and 0.4 GPa after 24 h). (F) Backscatter image to distinguish equilibrium fluid pools from quench bubbles (1200°C at 0.4 GPa after 15 min); equilibrium fluid pools contain chromite and quench to feathery quench phases whereas quench bubbles are voids after polishing. (G,H) Backscatter images of equilibrium fluid pools after controlled isobaric cooling from 1150 to 800°C by $1^{\circ} \text{min}^{-1}$; in G spiral skeletal chromite and in F euhedral pargasitic amphibole, clinopyroxene, and calcic plagioclase in a matrix of very fine-grained chromite microliths.

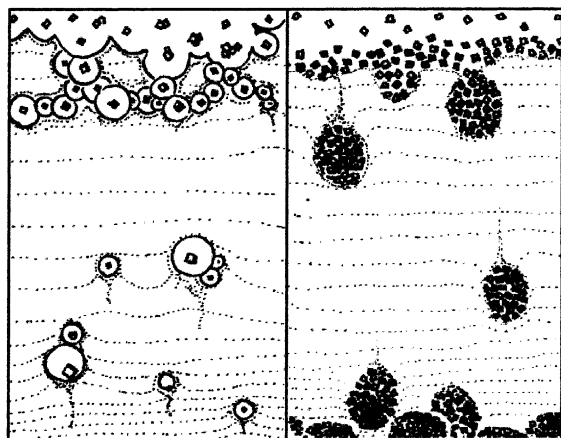


Fig. 4. Proposed two-stage mechanism of chromite nodule formation and chromite concentration. (A) Collection stage; fluid bubbles nucleate on dispersed chromite microliths and start floating in the denser basaltic melt, to collect to larger fluid pools near the top of the magmatic column. At this stage, efficient, small-scale separation of chromite from silicate phases by fluid wetting. (B) Settling stage; local chromite concentrations inside collected fluid pools have become large enough to exceed the density of the underlying and supporting basaltic melt. Development of 'downspouts' and formation of typical nodular chromite ore.

equilibrium with a basaltic melt, would crystallize during slow, near-equilibrium isobaric cooling. Upon opening, the fluid pools were found recrystallized to euhedral pargasitic amphibole, aluminous augitic clinopyroxene, labradoritic plagioclase, and skeletal chromite. Phlogopite was not observed, but this may reflect too high fluid–rock ratios in the experiments as compared to nature. By implication, the hydrous, negative crystal-shaped silicate inclusions in chromite represent the solute and the saline fluid inclusions described by Melcher et al. [28] the solvent, of a former magmatic fluid phase floating the chromite.

5. Platinum-group element (PGE) abundances in podiform chromite ore

Natural chromitites are often enriched in the refractory PGEs Os, Ir, and Ru, relative to basaltic melts [29,30]. PGE spectra of podiform chromitites, normalized to primitive mantle [31], are complementary to those of primitive basaltic

melts [32,33]. Conventionally, this is thought to reflect compatibility of Os, Ir, and Ru with magmatic oxide lattices [34,35]. In chromite ores, however, Os, Ir, and Ru form discrete alloys included in chromite [28,36–38] rather than occurring in solid solution. Quite possibly, many alloy inclusions may be secondary and may have formed by subsolidus volume exsolution of PGEs out of chromite but some may also be primary magmatic. In this case the melt would have to be oversaturated with discrete PGE alloys at the time of chromite flotation.

The PGE inventory of the convecting upper mantle is believed to reside in monosulfide liquid solution [39,40]. If during silicate melt segregation part of the mantle sulfide becomes entrained in the silicate melt [41] and dissolved during decompression [42], there is a good chance to oversaturate the basalt with respect to the least soluble PGEs, notably at low f_{O_2} [43]. For example, if we extrapolate Borisov and Palme's [44] Ir and Ru solubilities in FeO-bearing diopside-anorthite eutectic melt to FMQ-1 and 1200°C, we obtain solubility limits in these refractory PGEs of ~1.5 and 0.3 ppb, respectively. If all mantle

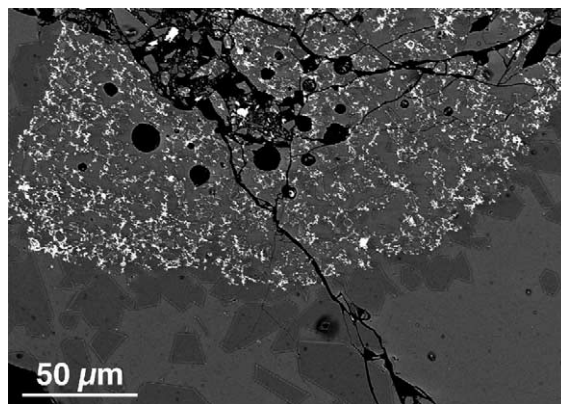


Fig. 5. Fractionation of Ir–Fe alloys between basaltic melt and water-rich fluid at 1200°C and 0.5 GPa, after 2 h (back-scatter image). The image shows an interface between an exsolved fluid pool (upper) and silicate melt (lower). The system is saturated with olivine phenocrysts residing in silicate glass (here mostly attached to the fluid–melt interface) and bright Ir–Fe alloys wholly contained by the former fluid pool. No PGE alloys observed in silicate glass. In PGE-oversaturated, conjugate basalt–fluid systems, PGE alloys will fractionate, along with chromite, into the fluid phase.

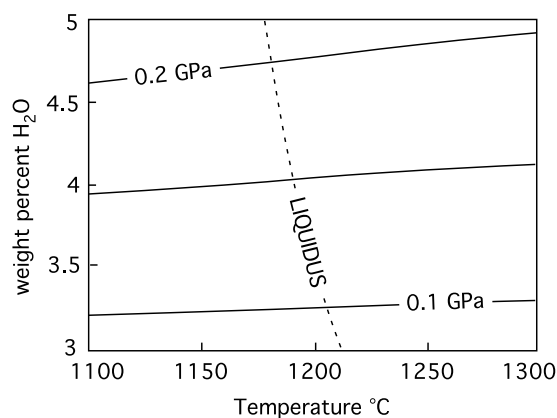


Fig. 6. Water solubility in basaltic melt, constructed using solubility data of Dixon et al. [47]. The dotted line is the basaltic liquidus at water saturation. For implications see text.

PGEs initially reside in sulfide [40], only about 10% of the residual mantle sulfide component needs be entrained to oversaturate a basalt with respect to the least soluble noble metals, and precipitate PGE ‘nuggets’.

To test how such nuggets would behave physically in a conjugate basalt–fluid system, we have carried out two experiments under identical experimental conditions as the chromite fractionation experiments (1200°C, 0.5 GPa) but this time only doped with Ir_2O_3 in the percentage concentration range. During experiment Ir_2O_3 reduced to micron-sized metallic Ir–Fe alloy nuggets, and after quenching all Ir–Fe nuggets were found concentrated in the fluid phase (Fig. 5). By implication, part of the refractory PGE inventory in podiform chromitites present as metal alloys may have been enriched by the same surface effects operating for chromite fractionation.

6. Conclusions

Podiform chromite deposits can only form in tectonic settings where basaltic melts have primary H_2O contents high enough to exsolve a water-rich fluid phase while decompressing inside the Earth’s mantle. The most plausible tectonic setting is a supra-subduction zone environment. Only here have primitive basalts the necessary water contents. By implication, massive podiform

chromitites are not expected to occur in oceanic lithosphere forming at mid-ocean ridges. MORB is too dry to exsolve a water-rich fluid at a depth in the lithostratigraphy where podiform chromitites would normally be found.

The identified process permits an independent estimate of whether up to 4% water, derived by analysis of melt inclusions in liquidus olivine from boninites [45,46], is a realistic pristine value for a primitive convergent margin melt (Fig. 6). The minimum lithostatic pressure resting on podiform chromite deposits can be calculated independently from crustal thicknesses in undeformed ophiolites. In Cyprus and Oman, two of the best-documented ophiolites with podiform mineralization, crustal thicknesses are around 8 and 6 km, respectively. Including the seawater column, these thicknesses translate into a lithostatic pressure at the MOHO of around 0.2 GPa, at the time of ore formation. The maximum amount of water a fluid-saturated basaltic melt can dissolve at this pressure is around 4 weight percent [47], in excellent agreement with the melt inclusion data.

Acknowledgements

We thank Eric Scherer, Miles Ormiston, Andrew Putnis, and David Green for critically reading the manuscript, Tom Sisson and Tom Wagner for reviewing the submitted version, and Bernie Wood and Patrice Hornibrook for editorial handling. Financial support by the German Research Council (Priority Program ‘Melts’) through Grant Ba 964/16 is greatly appreciated. [BW]

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