References

Bignall, G. and Browne, P.R.L.(1994) *Geothermics*, **23**, 645–58.

Browne, P.R.L., Bignall, G. and Mackenzie, K.M. (1994) *Trans. Geotherm. Res. Council*, **18**, 165–71.

Hutton, C.O. (1970) *Mineral. Mag.*, **37**, 939.

Lombardi, G. and Sposato, A. (1981) *Canad. Mineral.*, **19**, 403–7.

Palache, C., Berman H. and Frondel, C. (1951) *The system of mineralogy of James Dwight Dana and Edward Salisbury Dana, Yale University*, 1837–92. **2**, Wiley and Sons, New York.

Robinson, P.D., Fang, J.H. and Bloss, F. D. (1966) *Amer. Mineral.*, **51**, 1805–7.

Segnit, E.R. (1976) *Mineral. Mag.*, **40**, 642–4.

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Formation of chlor- and fluor-apatite in layered intrusions: A comment

IN a recent paper, Cawthorn (1994) presented a model for the formation of chlorapatite and fluorapatite in layered intrusions that differs from those presented by myself and my colleagues. In brief, Cawthorn suggests that apatite in intercumulus liquids initially crystallizes as a F-rich apatite, and that Cl-rich apatite forms mainly by reequilibration with trapped interstitial liquid. This process is analogous to that by which cumulus mafic minerals may become more Fe-rich on reequilibration with intercumulus liquids during solidification. In this interpretation, the high-Cl apatite that characterizes much of the lower stratigraphic sections of the Stillwater and Bushveld complexes can be explained solely as the result of more extensive reequilibration with intercumulus liquid than is seen in any other intrusions. In addition, Cawthorn suggests that the general decrease in the Cl/F ratio of apatite with stratigraphic height seen in many intrusions may simply represent a decreasing (trapped liquid)/(apatite) ratio with increasing stratigraphic height and need not require any fluid fractionation as suggested by myself and my colleagues.

In a review of an early draft of this paper, I pointed out several problems both in the representation of our earlier work and problems with the interpretation suggested by Cawthorn. None of these were addressed in the published manuscript, hence this comment. Here I will take note of two points of contention. The first has to do with a misinterpretation of my earlier work regarding the volatile content of the parent magma(s) of layered intrusions that contain high-Cl apatite such as the Stillwater and the Bushveld complexes. The second and more serious point has to do with the evidence for the role of reequilibration of intercumulus liquid as a significant cause for the stratigraphic decrease in the Cl/F ratio common to many intrusions.

Cawthorn misrepresents the assumptions and consequences of the model presented by Boudreau (1992). In this paper, it was suggested that degassing of fluid-saturated intercumulus liquids can give rise to fluid overpressures that can form pothole structures as these fluids escape from the crystal pile. It was suggested that potholes form in a manner analogous to pockmarks on the sea floor, which are also generally explained as gas-release structures (e.g. Hovland and Judd, 1988). In the quantitative expression of the model, water was used as an example of a volatile with a high solubility such that a large amount of fluid is exsolved during crystallization of the intercumulus liquid and hence represents a maximum overpressure that can develop; for CO_2-rich systems, the amount of fluid that evolves and the overpressures that can form are less (see also Tait *et al.*, 1989). Furthermore, it was also stated that intercumulus liquids need not be fluid-rich to begin with, but that stratigraphically higher intercumulus liquids can be enriched in volatiles as the deeper intercumulus liquids solidify and degas. That is, intercumulus liquids can be enriched by a vapour-refining process such that their volatile contents are much higher than when the liquid was initially trapped.

Although the model of Boudreau (1992) focused on pothole formation, Cawthorn misrepresented two important points of the model and its application to apatite chemistry. First, Cawthorn states that it is required that the intercumulus liquid was water-rich and that the initial magma had 4% H_2O, which is an amount that is unusually high for a basic or ultrabasic magma. However, as noted above, water is only used as an example of a soluble volatile species to define the maximum overpressure that might develop. Real magmatic fluids are mixtures of CO_2, H_2O and other volatiles. For Cl species in particular, their solubility in mafic systems is only very poorly known. Hence one can only look at end-member species like water and CO_2, for which there is at least some knowledge of their solubility. Second and more importantly, Cawthorn completely disregards the possibility of enrichment of intercumulus liquids in volatile concentrations during solidification and fluid separation of stratigraphically lower intercumulus liquids. Indeed, this was considered a key point of the model and explains why potholes developed only after some thickness of cumulates had accumulated; a region of enriched intercumulus liquid must develop as volatiles exsolved deep in the crystal pile accumulated in stratigraphically higher, hotter, and fluid-undersaturated intercumulus liquids near the crystallization front.

Thus, although Cawthorn may be correct in stating that the parent magmas have low volatile contents to begin with, this does not imply that the intercumulus liquids cannot be enriched in volatile components by mechanisms suggested by Boudreau and McCallum (1989). If intercumulus liquids can become enriched by such processes, then fluid fractionation of the halogens and its effect on apatite composition becomes an expected consequence.

A second and more serious point has do with the explanation for the development of Cl-rich apatite. Cawthorn suggests that intercumulus apatite initially crystallized as an F-rich apatite, perhaps even crystallized as a 'cumulus' mineral, and only became more Cl-rich as it reequilibrated with intercumulus liquid on cooling. Ignoring any possible variations in Cl/F ratio in parent liquids, Cl-rich apatite is therefore only likely to have formed where a large amount of trapped liquid was present relative to the amount of apatite. While the effect of reequilibration can lead to qualitative changes in the manner predicted by Cawthorn, it is unlikely to be the sole explanation for either the high-Cl apatite or the observed compositional stratigraphic trends for several reasons.

First, it is generally observed that the amount of intercumulus apatite present, whether fluorapatite or chlorapatite, is usually a function of the amount of other late-forming minerals such as quartz. For example, within the Stillwater complex, relatively abundant amounts of F-rich apatite are typically found in anorthosite of the Middle Banded series with large amounts of intercumulus quartz, and Cl-rich apatite is abundant in norites and gabbronorites in the Lower Banded series that also contain relatively abundant intercumulus quartz (e.g. Boudreau and McCallum, 1989). This suggests that apatite crystallized from the intercumulus liquid and that its abundance is a function of the amount of liquid present at apatite saturation. Apatite modal abundance also parallels stratigraphic trends for incompatible elements, the concentrations of which can be interpreted as being a function of the amount of trapped liquid. For example, within the Munni Munni complex, incompatible trace elements show a marked increase in the upper parts of the Ultramafic zone (e.g. Hoatson and Keays, 1989). Relatively Cl-poor apatite and other late-forming minerals such as quartz and biotite are rarely observed below this zone but are much higher within this incompatible element-enriched zone (Boudreau *et al.*, 1993).

Second, for the Critical Zone and Main Zones of the Bushveld Complex, the average Zr/P ratios are 0.10 and 0.26 and the Ba/P ratios are 0.43 and 0.86, respectively (Cawthorn, 1983). In contrast, the Cl/F ratio of intercumulus apatite of the Critical Zone is about twice that of the Main Zone (Boudreau *et al.*, 1993). The higher Zr/P and Ba/P ratios of the Main Zone are the exact opposite of those expected if the Cl/F were predominantly controlled by the apatite/trapped liquid ratio as suggested by Cawthorn (1994). Instead, the fact that P concentration tends to parallel Zr and Ba trends within each zone suggests that the amount of pore liquid controls the amount of apatite that eventually crystallizes from this liquid.

All this is not to say that there is no reequilbration with intercumulus liquid once apatite saturation has occurred. For example, the modal abundance of apatite relative to the amount of intercumulus liquid increases sharply as apatite becomes a cumulus mineral in the Skaergaard intrusion. Accompanying this change from an intercumulus to a cumulus mineral, the Cl content of apatite decreases from 0.35 to 0.05 wt.% and F increases from 2.65 to 3.64 wt.%

(Brown and Peckett, 1977). The higher Cl content of the intercumulus apatite of low modal abundance is consistent with more extensive reequilibration with interstitial liquid as suggested by Cawthorn. However, these changes in Cl content are relatively modest and in no instance has it been observed that one can go from relatively F-rich apatite to near end-member chlorapatite compositions (with apatite containing in excess of 6 wt.% Cl) by changing the amount of intercumulus liquid alone. The fact that Cawthorn presents no evidence that such a correlation exists, and that all existing data do not support such a correlation, points to the weakness of his conjecture on this point.

Furthermore, the requirement that Cl behaves incompatibly relative to F during crystallization of apatite requires that the magmas should become even more Cl-rich once apatite becomes a cumulus phase, assuming that apatite is the only phase fractionating the halogens (i.e. the magma is not also fluid-saturated). If this were the case, cumulus apatite should become more Cl-rich with stratigraphic height, much as the mafic minerals become more Fe-rich. This is not observed. For example, in the Skaergaard intrusion, apatite in the most fractionated rocks represented by the Sandwich Horizon approaches end-member fluorapatite composition and contains only modest amounts of Cl (Nash, 1976; Brown and Peckett, 1977). A much more striking case exists in the Bushveld intrusion, where cumulus apatite displays a general decrease in Cl/F ratio with height such that the stratigraphically highest cumulus apatites are the most Cl-poor, F-rich compositions of the complex (Boudreau *et al.*, 1993). This suggests that some additional phase (e.g. a fluid) must be fractionating the halogens to cause a reversal of the compositional trend expected by apatite fractionation alone.

In conclusion, disagreement with Cawthorn (1994) can be summarized as follows. First, a relatively 'dry' parent magma does not necessarily imply that the intercumulus liquid cannot develop high volatile concentrations. The volatile contents of the intercumulus liquid at any level within an intrusion can increase as fluids separating from underlying solidifying intercumulus liquids migrate upward and enrich the stratigraphically higher intercumulus liquids in volatile components, leading to progressively earlier fluid-saturation. Hence a decoupling of halogen compositional trends from major elements trends is an expected and observable consequence. Second, the suggestion that stratigraphic trends in the halogens is due primarily to apatite reequilibration with variable amounts of intercumulus liquid is not supported by any new or existing data. Indeed, the observation that the stratigraphic trend of decreasing Cl/F in cumulus apatite is the exact opposite of the expected trend if apatite alone were the fractionating agent. While Cawthorn is to be applauded for suggesting alternative interpretations, the fractionation of Cl and F in layered intrusions as exemplified by apatite chemistry still appears to require a fluid agent.

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References

Boudreau, A.E. (1992) Volatile fluid overpressure in layered intrusions and the formation of potholes. *Austral. J. Earth Sci.*, **39**, 277–87.

Boudreau, A.E., Love, C. and Hoatson, D.M. (1993) Variation in the composition of apatite in the Munni Munni complex and associated intrusions of the West Pilbara Block, Western Australia. *Geochim. Cosmochim. Acta*, **57**, 4467–77.

Boudreau, A.E. and McCallum, I.S. (1989) Investigations of the Stillwater complex: Part V. Apatites as indicators of evolving fluid composition. *Contrib. Mineral. Petrol.*, **102**, 138–53.

Boudreau, A.E. and McCallum, I.S. (1990) Low temperature alteration of REE-rich chlorapatite from the Stillwater complex, Montana. *Amer. Mineral.*, **75**, 687–93.

Boudreau, A.E., Meurer, W.P., Cawthorn, R.G. and Mathison, C.I. (1993) *Halogens in layered intrusions.* Geological Society of America Annual Conference, Boston, Massachusetts, October 1993. Abstracts with Programs, v. **25**, p. A372.

Brown, G.M. and Peckett, A. (1977) Fluorapatites from the Skaergaard intrusion, East Greenland. *Mineral. Mag.*, **41**, 227–32.

Cawthorn, R.G. (1983) Magma addition and possible decoupling of major- and trace-element behavior in the Bushveld Complex, South Africa. *Chem. Geol.*, **39**, 335–45.

Cawthorn, R.G. (1994) Formation of chlor- and fluor-apatite in layered intrusions. *Mineral. Mag.*, **58**, 299–306.

Hoatson, D.M. and Keays, R.R. (1989) Formation of platiniferous sulfide horizons by crystal fractionation and magma mixing in the Munni Munni layered intrusion, West Pilbara Block, Western Australia. *Econ. Geol.*, **84**, 1775–804.

Hovland, M. and Judd, A.G. (1988) *Seabed pockmarks and seepages: Impact on geology, biology and the marine environment.* Graham and Trotman, London, 293 pp.

Nash, W.P. (1976) Fluorine, chlorine and OH-bearing minerals in the Skaergaard intrusion. *Amer. J. Sci.*, **276**, 546–57.

Tait, S., Jaupart, C. and Vergniolle, S. (1989) Pressure, gas content and eruption periodicity of a shallow, crystallizing magma chamber. *Earth Planet. Sci. Lett.*, **92**, 107–23.

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