A CHLORINE ISOTOPE TRANSECT ACROSS THE SUDBURY IMPACT DEPOSITS REVEALS ENIGMATIC ISOTOPIC FRACTIONATION.

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Introduction: Volatile elements play an important role in a variety of cosmochemical and geochemical processes. As such, there has been significant interest in their abundance and isotopic composition.

Chlorine is an important element for tracing these processes because it is incompatible in nearly all minerals, extremely volatile, and strongly hydrophilic [1]. The Cl isotope composition ($^{37}Cl/^{35}Cl$) of meteoritic components, therefore, can provide useful information regarding the isotopic reservoirs that were present in the early Solar System and any secondary processes that may have occurred on different parent bodies (e.g., [2-4]). There is a relatively narrow range in the Cl isotope compositions of terrestrial, Martian, and chondritic meteorites ($\delta^{37}Cl \sim -6$ to $+4$‰) (e.g., [2,3,5,6]), with exceptions to this being the Moon and Vesta (up to $\sim +81$‰ and $\sim +40$‰, respectively) [4, 5, 7-10].

One hypothesis for the extreme Cl isotope fractionation observed on the Moon is degassing following large-scale (possibly even crust-breaching) impact events [7-9]. The role of hypervelocity impacts and impact-generated magmatism in the isotopic evolution of planetary materials, however, has been until recently an area of limited published research with the majority of works focusing on the effects of impact shock (e.g., [10-13]).

The ~ 1.85 Ga Sudbury impact crater [14] located in Ontario, Canada, is one of the three largest impact craters on Earth with good exposures of its impact melt sheet and overlying breccias [15,16]. The impact melt sheet, called the Sudbury Igneous Complex (SIC), is up to 5 km thick [17], with an estimated original volume of $>10^4$ km^3 [18], and differentiated. Recent work demonstrated evaporative loss and isotope fractionation of the moderately volatile element zinc and suggest melt sheets produced by impacts could have a significant effect on the Earth's volatile inventory [19].

In this study we investigate the abundance and isotopic composition of Cl as well the water abundance of apatite from the SIC and the overlying crater-fill to test the hypothesis that large-scale impacts may have generated the extensive Cl isotopic fractionation observed on the Moon.

Samples: A total of 10 samples were selected from a detailed stratigraphic sampling of the Sudbury structure: two norites representing the lower melt sheet (SUD9497-4, SUD9497-5), a quartz gabbro representing the middle melt sheet (SUD9497-6), and three sections of granophyre representing the upper melt sheet (SUD9496-7, -8, and SUD9597-1). Four samples from the base of the overlying Onaping impact melt breccia were also analysed (SUD9597-2, -3, -4, -6).

Methods: The Cl abundance and isotopic composition along with water content in apatite were measured using the Cameca ims 1280 ion-microprobe at the University of Hawai'i at Mānoa. High [Cl] apatite were measured with an ~ 1.4 nA Cs primary beam using Faraday cups, whereas lower [Cl] apatite were measured using electron multipliers using a 50 pA Cs primary beam. In both protocols, Cl-isotopes were measured simultaneously, while other masses were measured with peak-jumping. The primary beams were rastered over 7×7 μm and 5×5 μm, respectively. To minimise potential contamination at lower beam currents, electronic gating was used to collect ions from the inner 3×3 μm. Apatite standards used in this study were from [20].

Results and Discussion: A total of 64 measurements were collected from 48 individual apatite grains across the suite of samples. Chlorine abundance across all samples displays significant variation across several orders of magnitude from 118 to 15,773 ppm, with the lowest and highest [Cl] seen in the Onaping Formation (SUD9597-6 and SUD9597-4, respectively) (**Fig. 1**). Within the SIC, the quartz gabbro of the middle melt sheet (SUD9497-6) has the most consistent [Cl] between $\sim 4,000$ and 9,200 ppm and the greatest variation is observed in the norites of the lower melt sheet ($\sim 1,300$ to 14,400 ppm Cl).
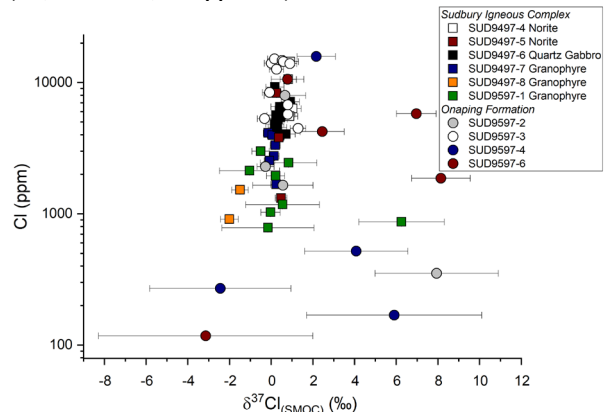
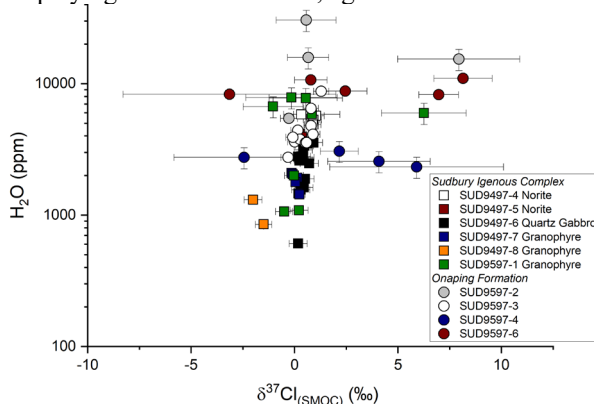**Figure 1:** *Chlorine isotope composition vs. chlorine content (ppm).*

The Cl isotopic compositions range from -3.14 ± 5.14‰ to $+8.15 \pm 1.41$‰ (2σ), with the largest variation again observed in the Onaping Formation. The lower and middle melt sheet of the SIC display consistent isotope compositions around 0‰. Apatite grains from the upper melt sheet display a similar variation to that of the Onaping Formation (-1.03‰ to $+6.26$‰) with the stratigraphically highest sample (SUD9597-1) displaying the largest variation within the SIC. This trend of increasing variation with stratigraphic succession is observed in the weighted average uncertainties (**Fig. 2**). Weighted averages for the SIC, Onaping, and the entire sample set, however, are all ~0‰.
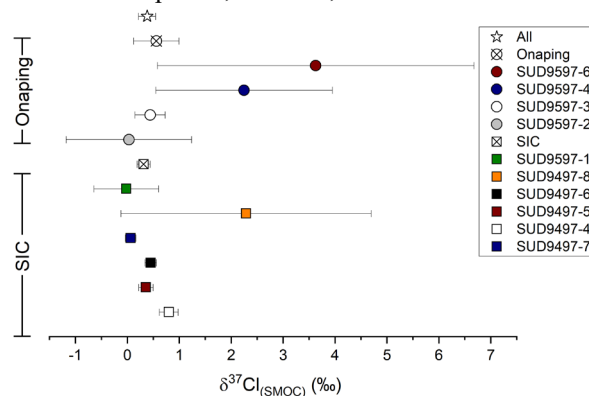
Figure 2: *Chlorine isotope composition as a function of stratigraphic succession. Weighted averages for the entire SIC, Onaping, and entire dataset are also included for reference.*

The water content of samples studied here defines a larger variation than that of Cl, ranging from 607 to 30,521 ppm H_2O (**Fig. 3**) with both the lower melt sheet and the stratigraphically lowest Onaping sample displaying the most variation, again.

Figure 3: *Chlorine isotope composition vs. water content (ppm).*

Overall, there appears to be a minor correlation between [Cl] and δ^{37}Cl values with lower [Cl] typically showing the most fractionation in both directions away from 0‰. No correlation, however, is observed between $[H_2O]$ and δ^{37}Cl values. Given that both ^{37}Cl-rich and ^{37}Cl-poor isotope signatures are observed at low [Cl], pure magmatic degassing cannot be used to fully explain the dataset. The appreciable amounts of water also likely buffers any significant fractionation from degassing such as that observed on the Moon where metal chlorides are the dominate phase for Cl degassing and the cause of fractionation [1,21].

One possible explanation relates to the extensive hydrothermal system that existed after the impact (e.g. [22-24]). Fractionations up to 9‰, broadly similar to those seen in this study, have been observed at high-temperature fumaroles associated with crater lakes [1]. These values were attributed to a distillation process in which ^{35}Cl is preferentially incorporated as a aqueous chloride species, leaving the HCl(g) with ever-increasing δ^{37}Cl values.

Conclusion: Data from this study show that the apatite in both the SIC and Onaping Formation display Cl isotope signatures similar to that of Mars with more elevated values typically higher up the stratigraphic sequence. A modest amount of fractionation observed (up to +8.15‰) can be explained by a liquid-vapor hydrothermal mechanism [1]. This could imply that simply having voluminous melt, post-impact, may not be enough to generate the significant fractionation observed on the Moon.

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