

**WATER EXTRACTS FROM MURCHISON CM2 CHONDRITE: TRACE METALS AND MAJOR IONS.**

M. Yu. Zolotov<sup>1</sup>, N. B. Zolotova<sup>1</sup> and S. J. Romaniello<sup>1</sup>, <sup>1</sup>School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-1404, USA. E-mail: zolotov@asu.edu

**Introduction:** The composition of water-soluble species in chondrites could constrain aqueous chemistry on their parent asteroids and other bodies (e.g. Europa) that accreted altered chondrites [e.g. 1,2]. The low-temperature ( $\leq \sim 25$  °C) aqueous alteration of the parent body of CM2 carbonaceous chondrites led to formation of tochilinite, cronstedtite, serpentine, magnetite, calcite and gypsum. Chemical and isotopic composition of these phases could reflect water/rock (*W/R*) ratio, *pH* and *Eh* of aqueous environments. High-solubility chlorides and Na/Mg sulfates could characterize late brines, and sulfates reflect an action of strong oxidants. Although chlorides and Na/Mg sulfates have not been reported in solid-state studies of CM2 samples, their presence is suggested from the composition of water extracts. Here we report concentrations of trace metals, major cations and anions, and dissolved inorganic C (DIC) in a series of high *W/R* extracts from the Murchison CM2 chondrite.

**Methods and results:** A 100 mg sample of Murchison was powdered under dry trace-metal-free conditions. A series of 3 leachates were conducted using different masses of powder (1.653, 5.569 and 11.350 mg) and 20 g deionized oxygen-free water degassed with Ar. The extraction occurred in metal-free plastic vials in the Ar atmosphere over 21 h at 22 °C. Centrifuged solutions were filtered with 0.2  $\mu\text{m}$  pre-cleaned PES filters. The measured *pH* of leachates and a blank solution was  $6.4 \pm 0.1$ . For comparison, a complete  $\text{HNO}_3$ -HCl-HF digest and carbonate analyses were performed on two separate  $\sim 10$  mg aliquots of the powdered sample. All of the extracts and the bulk sample were analyzed by Q-ICP-MS. In the bulk composition (ppm), Na, 4.55E+3; Mg, 1.29E+5; Al, 1.23E+4; K, 4.73E+2; Ca, 1.30E+4; V, 70; Cr, 2.9E+03; Mn, 1.74E+3; Fe, 2.55E+5; Co, 637; Ni, 1.40E+04; Ga, 5.36; Rb, 1.80; Sr, 11.0; Mo, 1.14; Ba, 3.16; Re, 0.041. Concentrations of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and anions in extracts were determined by ion chromatography, IC. The measured DIC concentration in leachates concurs with the bulk sample value for inorganic C (0.15 – 0.22 wt% C, preliminary data). The measured total C content is  $1.86 \pm 0.2$  wt%.

**Discussion:** Our data indicate complete leaching of Cl and a major dissolution of sulfates. The bulk composition, sulfate S (0.46 – 0.54 wt%) and Cl ( $219 \pm 13$  ppm) contents agree with previous data [e.g. 3-5]. The molal composition of leachates Cl ( $0.040 \pm 0.005$ ), Na ( $0.71 \pm 0.10$ ), Mg ( $0.67 \pm 0.15$ ), Ca ( $0.63 \pm 0.15$ ) and K ( $0.027 \pm 0.007$ ) (IC data) relative to  $\text{SO}_4^{2-}$  concur with Murchison extracts at *W/R* = 200 [1] but reveals higher Ca and Mg contents at *W/R* of  $1.8 \times 10^3$  –  $1.2 \times 10^4$ . The DIC content (molal concentrations of  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  are roughly comparable), the charge balance constraints and the similarity between bulk carbonate and leached DIC content imply a significant dissolution of carbonates. Under these conditions, calcite and gypsum are undersaturated and likely undergo dissolution, especially at higher *W/R* ratios. Therefore, the composition of water leachates could reflect that of chlorides, Mg/Na sulfates, putative Na carbonates, and at least some Ca carbonates and sulfates.

The most abundant leached species are inorganic C, sulfate and Na. The extract/bulk ratios for Na, Re and Mo (0.75, 0.31, 0.14, respectively) do not depend on the *W/R* ratio and suggest complete dissolution of element bearing salts. The data on Re and Mo suggest their presence in high-solubility oxidized forms such as perrhenate and molybdate and indicate parent body oxidation of corresponding sulfides by oxidants that altered FeS to sulfates. The apparent lack of high-solubility Cr(VI) compounds sets an upper limit for  $f\text{O}_2$  in parent body solutions.

Concentrations (ppm) of Mn (8.7E-4), Co (1.7E-4) and Ni (1.9E-2) in solution are independent on the *W/R* ratio and suggest saturation with respect to low-solubility oxides and sulfides. For some elements, the extract/bulk ratios systematically decrease at lower *W/R*. We report a range of the ratios for K (0.76 – 0.51), Ca (0.42 – 0.27), Sr (0.45 – 0.26), Rb (0.37 – 0.22), Mg ( $3.0\text{E}-2$  –  $2.2\text{E}-2$ ), Ba ( $3.5\text{E}-2$  –  $1.2\text{E}-2$ ), Ga ( $2.0\text{E}-2$  –  $1.3\text{E}-2$ ), Al ( $9.3\text{E}-3$  –  $3.2\text{E}-3$ ), V ( $1.2\text{E}-3$  –  $1.0\text{E}-3$ ), Cr ( $5.5\text{E}-4$  –  $3.2\text{E}-4$ ), Fe ( $2.3\text{E}-5$  –  $1.2\text{E}-5$ ). Less sulfate S is leached at lower *W/R* (0.46 wt%) than at higher *W/R* (0.54 wt%). These data imply incomplete dissolution of solids, less efficient dissolution of higher-mass samples and low-solubility solids due to kinetic effects. These data represent only *W/R* ratios and duration of these extraction runs. Mg extraction reflects dissolution of Mg salts and preservation of its majority in low-solubility silicates. The matching leaching factors of Ca and Sr suggest release of Sr from calcite and gypsum. The data for Cr and Fe suggest approaching saturation at lower *W/R* ratios.

In summary, the coordinated use of ICP-MS, IC and DIC analyses of water extracts from carbonaceous chondrites falls at variable *W/R* ratios provides information on the composition of high- and low-solubility phases and constrains the aqueous chemistry and redox conditions on parent bodies at the time of aqueous alteration.

**References:** [1] DuFresne E. R. and Anders E. (1962) *Geochimica et Cosmochimica Acta* 26:1085–1114. [2] Fanale F. P. et al. (2001) *Journal of Geophysical Research* 106:14595–14600. [3] Makishima A. and Nakamura E. (2006) *Geostandards and Geoanalytical Research* 80:245–271. [4] Labidi J. et al. (2017) *Geochimica et Cosmochimica Acta* 196:326–350. [5] Dreibus G. et al. (1979) *Physics and Chemistry of the Earth* 11:33–38.