## CLAYS BEYOND EARTH

RALPH E. MILLIKEN<sup>1</sup> AND DAVID L. BISH<sup>2</sup>

<sup>1</sup> Department of Civil Engineering and Geological Sciences, University of Notre Dame, IN 46556, USA
<sup>2</sup> Department of Geological Sciences, Indiana University, 1001 East 10th Street, Bloomington, IN 47405-1405, USA

Even the most casual observer will recognize that rocks transform to clay minerals over time on Earth, and clay minerals have played a particularly important role in the geologic evolution of our planet as well as the evolution of human civilization. Clay minerals, however, have also played an important role elsewhere in our Solar System, and they provide some of the best evidence of aqueous processes during time periods not accessible in Earth's rock record. The wealth of new data acquired using a variety of remote sensing techniques on planetary missions, coupled with detailed laboratory studies of meteorites, have increased awareness of this fact over the past several decades. The recent renewed interest in clay minerals formed beyond Earth led to a session on new developments in the study of extraterrestrial clay minerals during the 14<sup>th</sup> International Clay Conference in Castellaneta Marina, Italy, in 2009, and this issue of Clays and Clay Minerals presents several papers that resulted from that session.

The number and variety of minerals have increased during the history of our Solar System, yet clay minerals clearly have existed since at least the time of planetary accretion (e.g. Hazen et al., 2008). The class of meteorites known as carbonaceous chondrites (C class) represents material from undifferentiated bodies, and the mineralogy of these samples (most notably meteorites within the CI and CM groups) indicate aqueous alteration at ~4.56 Ga (see Brearley and Jones, 1998, and Brearley, 2006, for reviews on this topic). Velbel and Palmer (2011) present a review of serpentines in CM chondrites in the context of understanding the extent of this aqueous alteration based on serpentine chemistry. In addition, they explore the difficult task of distinguishing between chemical imprints caused by terrestrial weathering/contamination and those caused by aqueous processes on the meteorite parent body. This is a nontrivial task, yet one that is crucial for understanding the true extent and variability of aqueous processes during the infancy of our Solar System.

One of the more recent developments in the area of extraterrestrial clays has been the widespread detection of clay minerals on the surface of Mars (*e.g.* Poulet *et al.*, 2005; Bibring *et al.*, 2006; Murchie *et al.*, 2009). In

DOI: 10.1346/CCMN.2011.0590400

contrast to the C chondrites, the ages of clay mineral deposits that have been identified from orbit on Mars are naturally more poorly constrained. However, many of these deposits are found within the oldest parts of the crust, dated by crater counting to have formed >3.5 Ga, and clay minerals are conspicuously absent in younger terrains, suggesting a regional or global change in environmental conditions (Poulet et al., 2005; Bibring et al., 2006). Some of these clay mineral detections are associated with sedimentary rocks and may indicate transport or formation in fluvial-alluvial or lacustrine settings (e.g. Grant et al., 2008; Ehlmann et al., 2008; Milliken and Bish, 2010). However, distinguishing between detrital and authigenic clays is a tricky business on Earth, let alone on another planet when limited only to remote techniques. Bristow and Milliken (2011) review the attributes associated with authigenic clay formation in terrestrial lacustrine environments and discuss how such deposits might be identified on Mars. As is the case for Earth, clay mineral deposits on Mars are quite diverse. In contrast to low-temperature sedimentary environments, the composition, geologic setting, and mineral assemblages of other Martian clay deposits may be more indicative of localized low-grade metamorphism or hydrothermal alteration, as discussed by Ehlmann et al. (2011).

Visible-near infrared reflectance (VNIR) spectra of the Martian surface acquired from orbit have been interpreted to indicate the presence of a variety of 7, 10, and 14 Å clay minerals, including kaolin/serpentine group minerals, smectite, and chlorite (Mustard et al., 2008; Bishop et al., 2008; Ehlmann et al., 2010). However, accurate identification of specific minerals, their chemical compositions, and modal abundances of mineral mixtures and complex surfaces using reflectance spectroscopy is hampered by multiple scattering effects and nonlinear absorption processes. Therefore, accurate identification of subtle changes in clay mineral chemistry or modal mineralogy requires that spectral models be tested with laboratory experiments. Bishop et al. (2011) use laboratory data to examine differences in the VNIR spectral properties of montmorillonite and beidellite, both of which may be present on Mars, whereas McKeown et al. (2011) examine reflectance spectra of mixtures composed of clay minerals and other siliceous phases. Together, these studies indicate that the clay mineralogy of Mars is probably more complex than our current understanding suggests, and they underscore the importance of theoretical and laboratory work for proper interpretation of remotely acquired reflectance spectra of clay-bearing deposits.

This collection of papers about extraterrestrial clay minerals, along with numerous other papers written in recent years, highlights the fact that much work remains to be done on this topic in order to understand the specific origins, compositions, and geologic implications of these clay minerals. The hope in presenting these papers together in one issue is to stimulate interest and discussion amongst the broader community of scientists who are interested in clay minerals and continue to promote interaction between researchers studying clays on Earth and those studying clays on other planetary bodies. The vast majority of our knowledge about clay minerals, their formation mechanisms, compositions, and long-term stability is grounded in the study of terrestrial examples under Earth-relevant conditions, and this provides the necessary foundation for initial interpretations of clays discovered in extraterrestrial environments. However, the diversity and great antiquity of clays in meteorites and on Mars provide a record of geologic processes and natural long-term stability experiments that are not preserved in the terrestrial rock record, so the extraterrestrial clays may have just as much to tell us about clay minerals found on Earth.

## REFERENCES

- Bibring, J.-P., Langevin, Y., Mustard, J.F., Poulet, F., Arvidson, R., Gendrin, A., Gondet, B., Mangold, N., Pinet, P., Forget, F., and the OMEGA Team (2006) Global mineralogical and aqueous Mars history derived from OMEGA/Mars Express data. *Science*, **312**, 400-404.
- Bishop, J.L, Noe Dobrea, E.Z., McKeown, N.K., Parente, M., Ehlmann, B.L., Michalski, J.R., Milliken, R.E., Poulet, F., Swayze, G.A., Mustard, J.F., Murchie, S.L., and Bibring, J.-P. (2008) Phyllosilicate diversity and past aqueous activity revealed at Mawrth Vallis, Mars. *Science*, **321**, 830–833.
- Bishop, J.L., Gates, W.P., Makarewicz, H.D., McKeown, N.K., and Hiroi, T. (2011) Reflectance spectroscopy of beidellites and their importance for Mars. *Clays and Clay Minerals*, 59, 378–399.
- Brearly, A.J. (2006) The action of water. Pp. 587-624 in: *Metorites and the Early Solar System II* (D.S. Lauretta and H.Y. McSween, editors). University of Arizona Press, Tucson, Arizona, USA.
- Brearley, A.J. and Jones, R.H. (1998) Chondritic meteorites. Pp 3-1-3-398 in: *Planetary Materials* (J.J. Papike, editor). Reviews in Mineralogy, 36, Mineralogical Society of America, Washington, D.C.

Bristow, T.F. and Milliken, R.E. (2011) Terrestrial perspective

on authigenic clay mineral production in ancient Martian lakes. *Clays and Clay Minerals*, **59**, 339–358.

- Ehlmann, B.L., Mustard, J.F., Fassett, C.I., Schon, S.C., Head III, J.W., Des Marais, D.J., Grant, J.A., and Murchie, S.L. (2008) Clay minerals in delta deposits and organic preservation potential on Mars. *Nature Geoscience*, 1, 355-358.
- Ehlmann, B.L, Mustard, J.F., and Murchie, S.L. (2010) Geologic setting of serpentine deposits on Mars. *Geophysical Research Letters*, **37**, L06201.
- Ehlmann, B.L., Mustard, J.F., Clark, R.N., Swayze, G.A., and Murchie, S.L. (2011) Evidence for low-grade metamorphism, hydrothermal alteration, and diagenesis on Mars from phyllosilicate mineral assemblages. *Clays and Clay Minerals*, **59**, 359–377.
- Grant, J.A., Irwin, R.P., Grotzinger, J.P., Milliken, R.E., Tornabene, L.L., Mcewen, A.S., Weitz, C.M., Squyres, S.W., Glotch, T.D., and Thomson, B.J. (2008) HiRISE imaging of impact megabreccia and sub-meter aqueous strata in Holden Crater, Mars. *Geology*, 36, 195–198.
- Hazen, R.M., Papineau, D., Bleeker, W., Downs, R.T., Ferry, J.M., McCoy, T.J., Sverjensky, D.A., and Yang, H. (2008) Mineral evolution. *American Mineralogist*, **93**, 1693–1720.
- McKeown, N.K., Bishop, J.L., Cuadros, J., Hillier, S., Amador, E., Makarewicz, H.D., Parente, M., and Silver, E.A. (2011) Interpretation of reflectance spectra of clay mineral-silica mixtures: Implications for Martian clay mineralogy at Mawrth Vallis. *Clays and Clay Minerals*, **59**, 400–415.
- Milliken, R.E. and Bish, D.L. (2010) Sources and sinks of clay minerals on Mars. *Philosophical Magazine*, 90, 2293-2308.
- Murchie, S.L., Mustard, J., Ehlmann, B., Milliken, R.E., Bishop, J., McKeown, N., Noe Dobrea, E., Seelos, F., Buczkowski, D., Wiseman, S., Arvidson, R., Wray, J., Swayze, G., Clark, R., Des Marais, D., McEwen, A., and Bibring, J.-P. (2009) A synthesis of Martian aqueous mineralogy after 1 Mars year of observations from the Mars Reconnaissance Orbiter. *Journal of Geophysical Research*, **114**, E00D06.
- Mustard, J.F., Murchie, S.L., Pelkey, S.M., Ehlmann, B.L., Milliken, R.E., Grant, J.A., Bibring, J.P., Poulet, F., Bishop, J., Dobrea, E.N., Roach, L., Seelos, F., Arvidson, R.E., Wiseman, S., Green, R., Hash, C., Humm, D., Malaret, E., McGovern, J.A., Seelos, K., Clancy, T., Clark, R., Des Marais, D., Izenberg, N., Knudson, A., Langevin, Y., Martin, T., McGuire, P., Morris, R., Robinson, M., Roush, T., Smith, M., Swayze, G., Taylor, H., Titus, T., and Wolff, M. (2008) Hydrated silicate minerals on Mars observed by the Mars Reconnaissance Orbiter CRISM instrument. *Nature*, 454, 305–309.
- Poulet, F., Bibring, J.P., Mustard, J.F., Gendrin, A., Mangold, N., Langevin, Y., Arvidson, R.E., Gondet, B., Gomez, C., and Omega, T. (2005) Phyllosilicates on Mars and implications for early Martian climate. *Nature*, 438, 623–627.
- Velbel, M.A. and Palmer, E.E. (2011) Fine-grained serpentine in CM2 carbonaceous chondrites and its implications for the extent of aqueous alteration on the parent body: A review. *Clays and Clay Minerals*, **59**, 416–432.